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FINITE RATE EVAPORATION  
O. CRYOGENIC HYDROGEN  
IN TWO-PHASE AIR  
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R. Edelman and H. Rosenbaum

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ABSTRACT

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A theoretical study of two-phase continuum flow of hydrogen and air, for a given range of initial conditions is presented. Assumptions include; (1) condensed phases form a dilute suspension of spherical particles in the gas phase, (2) finite rate evaporation of condensed hydrogen at uniform particle temperature with film type heat and mass transfer, (3) equilibrium air condensation, (4) one-dimensional, globally-inviscid flow at uniform pressure, (5) negligible relative velocity of gas and condensed phases. Of special interest is the method employed in calculating the two-phase boundary and subsequent condensation of the air during the hydrogen evaporation process. This involves assuming the presence of an arbitrarily small mass fraction of condensed air when the two-phase boundary for the air is crossed and permits the calculation of the multiphase Gibbs potentials which are expressed in terms of mass fractions associated with each phase present. The ten (10) parameters of the problem are in six (6) mass fractions for the  $O_2$ ,  $N_2$ , and  $H_2$ ; the hydrogen particle temperature; the two-phase air and gas phase hydrogen temperature; the particle radius, and the overall degree of vaporization. The results indicate evaporation times on the order of  $10^{-5}$  sec. for  $1\mu$  radius particles, for the range of conditions of interest here.

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## FINITE RATE EVAPORATION OF CRYOGENIC HYDROGEN IN TWO-PHASE AIR

### I. INTRODUCTION

In Reference 1 a general analysis for the viscous flow of a multi-component-multiphase system is developed and applied to a low temperature hydrogen jet issuing into air. The jet was assumed in phase equilibrium on the basis that an elemental particle of the mixture was not subjected to rapid temperature changes as it moved through the mixing region. Furthermore, the equilibrium assumption reduces the mathematical complexity leading to a relatively straight forward means for calculating this important limiting case. A basic feature of the equilibrium condition is that the condensed hydrogen present in the exit plane of the jet must flash to vapor on mixing with the air. This occurs in virtue of the decrease in hydrogen pressure during mixing at a constant mixture pressure.

The purpose of the present investigation is to examine some non-equilibrium behavior in the two-phase hydrogen-air system. In particular, the non-equilibrium hydrogen evaporation will be studied. The air, however, is assumed to condense in equilibrium. Thus, the study may be termed a "partial equilibrium" analysis. In order to focus attention on the non-equilibrium behavior a simple constant pressure, globally inviscid stream



tube is chosen for the flow configuration. The condensed hydrogen is assumed to be a cloud of spherical particles having a uniform size. Furthermore, the cloud is assumed to form a dilute (non-interacting) suspension in the gas phase. The hydrogen is injected uniformly across the stream tube and at the air velocity. This together with the constant pressure condition precludes dynamic non-equilibrium between the phases. Thus, with prescribed initial thermodynamic coordinates and particle sizes, the time history for hydrogen evaporation can be determined based on appropriate rate laws for heat and mass transfer.

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## II. ANALYSIS:

The general conservation equations forming the basis for the present analysis are given below. For a detailed account of their development, the reader is referred to Reference 1. In the absence of chemical reactions, we have:

### Continuity of Mass:

Global:

$$\nabla \cdot (\rho_g V_g + \sum_i \rho_{p_i} V_{p_i}) = 0 \quad (1)$$

$i^{\text{th}}$  Condensed Phase:

$$\nabla \cdot \rho_{p_i} \underline{V_{p_i}} = \nabla \cdot \rho_p V_{p_i} X_{p_i} = -\dot{W}_{v_i} \quad (2)$$

where,

$$X_{p_i} = \frac{\rho_{p_i}}{\rho_p} \quad (3)$$

$i^{\text{th}}$  Gas Phase:

$$\nabla \cdot \rho_g \underline{V_g} Y_{v_i} = \dot{W}_{v_i} - \underline{j_{v_i}} \quad (4)$$

where,

$$Y_{v_i} = \frac{\rho_{g_i}}{\rho_g} \quad (5)$$

Momentum:

Global:

$$\rho_g \underline{V}_g \cdot \nabla \underline{V}_g + \sum_i \rho_{p_i} \underline{V}_{p_i} \cdot \nabla \underline{V}_{p_i} = \nabla \cdot \underline{\Pi}_g + \sum_i \dot{W}_{p_i}^F (\underline{V}_{p_i} \cdot \underline{V}_g) \quad (6)$$

 $i^{\text{th}}$  Condensed Phase:

$$\rho_{p_i} \underline{V}_{p_i} \cdot \nabla \underline{V}_{p_i} = f_{(\sum V_j) p_i} \quad (7)$$

where,  $f_{(\sum V_j) p_i}$  denotes the total gas phase force acting on the  $i^{\text{th}}$  condensed species.

Energy:

Global:

$$\begin{aligned} \nabla \cdot \left[ \rho_g \left[ h_g + \frac{\underline{V}_g \cdot \underline{V}_g}{2} \right] \underline{V}_g + \sum_i \rho_{p_i} \left( h_{p_i} + \frac{\underline{V}_{p_i} \cdot \underline{V}_{p_i}}{2} \right) \underline{V}_{p_i} \right] \\ = - \nabla \cdot \underline{q}_g + \nabla \cdot (\underline{\tau}_g \cdot \underline{V}_g) - \sum_i \nabla \cdot \underline{j}_{p_i} h_{p_i} \end{aligned} \quad (8)$$

 $i^{\text{th}}$  Condensed Phase:

$$\rho_{p_i} \underline{V}_{p_i} \cdot \nabla h_{p_i} = Q_{(\sum V_j) p_i} - \dot{W}_{p_i} L_i \quad (9)$$

The reduction of the above system of equations for the present application involves the following conditions which must be satisfied.

(1) Viscosity, heat conductivity, and diffusion on the global scale are negligible, i.e.,  $\mu_g = K_g = D_{i,j} \approx 0$  so that  $\underline{\tau}_g$ ,  $\underline{q}_g$  and  $\underline{j}_{p_i}$  are zero, respectively. (2)  $\underline{V}_{p_i} = \underline{V}_g$ .

The constant pressure condition together with the injection of hydrogen at the air velocity is satisfied for zero velocity lag throughout the entire process. This affords a simplification in that Eq. 's 6 and 7 are identically

satisfied with  $\underline{V}_{p_i} = \underline{V}_t$  constant.

Returning to the remaining governing equations we have:

Global Continuity:

$$\nabla \cdot \rho_m \underline{V} = 0 \quad (10)$$

where,

$$\sum_i \rho_{p_i} = \rho_p \quad (11)$$

and

$$\rho_m = \rho_g + \rho_p \quad (12)$$

Applying the Divergence Theorem to Eq. 10 over a volume of length,  $ds$ , and cross-sectional area,  $A$ , gives:

$$\frac{d}{ds} (\rho_m A V) = 0 \quad (13)$$

Note that  $V$  is constant so that  $\rho_m A$  is constant.

$i$ th Condensed Phase:

Eq. 2 becomes:

$$\frac{d}{ds} (A V \rho_p x_i) = - \dot{W}_{v_i} A \quad (14)$$

$i$ th Gas Phase:

Eq. 4 becomes:

$$\frac{d}{ds} (A V \rho_g Y_i) = \dot{W}_{v_i} A \quad (15)$$

It is convenient to introduce a new variable to replace  $\beta_p$  and  $\beta_g$ . In this regard, we define the "degree of vaporization" given by:

$$z = \frac{\rho_g}{\rho_m} \quad (16)$$

which denotes the ratio of total gas phase mass to the total mass.

Furthermore, the area,  $A$ , may be eliminated via Eq. 13. Thus

Eq. 14 becomes:

$$\rho_m \frac{d[(1-z)X_i]}{dt} = -\dot{W}v_i \quad (17)$$

where  $V = \frac{ds}{dt}$  Eq. 15 becomes:

$$\rho_m \frac{dzY_i}{dt} = \dot{W}v_i \quad (18)$$

Now, Eq.'s 17 and 18 yield the conservation of the total mass of species  $i$ :

$$Y_i z + X_i(1-z) = \text{const.} = B_i \quad (19)$$

In virtue of the equilibrium condition for  $O_2$  and  $N_2$  the continuity Equations, 17 and 18, for  $O_2$  and  $N_2$  are replaced by equilibrium relations. Thus, for hydrogen, we have:

$$\rho_m \frac{d[(1-z)X_{H_2}]}{dt} = -\dot{W}v_{H_2} \quad (20)$$

where as for  $O_2$  and  $N_2$  we have the equilibrium relations:

$$Y_i = \frac{\beta_i K_{fi}}{[z K_{fi} + (1-z) \frac{w_{g2}}{w_{F2}} (1 - X_{H_2} \frac{w_{F2}}{w_{H_2}})]} = 0 \quad (21 a, b)$$

and,

$$X_i - \frac{B_i \frac{w_{gs}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}})}{\left[ 3 \kappa_{fi} + (1 - 3) \frac{w_{gs}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) \right]} = 0 \quad (22 \text{ a, b})$$

for  $i = O_2$  and  $N_2$ . A brief development of these relations is given in

Appendix II.

In addition, for each phase, we have:

Gas Phase:

$$\sum_j Y_j = 1 \quad (23)$$

Condensed Phase:

$$\sum_j X_j = 1 \quad (24)$$

where:  $j = O_2, N_2$  and  $H_2$

Eq. 's 20, 21 a, b, 22 a, b, 23 and 24 may be regarded as expressing conservation of mass for the mixture and the species in each phase.

An **auxiliary** relation required for the hydrogen particle radius is deduced from the conservation of hydrogen mass for a single particle.

This is given by:

$$\frac{dr_p}{dt} = - \frac{r_p}{3\rho_{FH_2}} \dot{w}_{FH_2} \quad (25)$$

where the hydrogen density,  $\delta_{H_2}$ , takes on constant values over prescribed ranges of temperature.

Energy:Global:

Since the flow is inviscid on the global scale, Eq. 8 becomes:

$$\nabla \cdot \left[ (\rho_g h_g + \rho_f h_f) \underline{V} + \rho_m \frac{\underline{V} \cdot \underline{V}}{2} \underline{V} \right] = 0 \quad (26)$$

and in virtue of the constant velocity condition this equation is merely a statement of constant global static enthalpy:

$$\sum_i \left[ Y_{O_2} h_{g_{O_2}} + Y_{H_2} h_{g_{H_2}} + Y_{H_2O} h_{g_{H_2O}} \right] + (1-\beta) \left[ X_{O_2} h_{p_{O_2}} + X_{H_2} h_{p_{H_2}} + X_{H_2O} h_{p_{H_2O}} \right] = C \quad (27)$$

$C = \text{constant}$

i<sup>th</sup> Condensed Phase:

In virtue of the equilibrium condition for the air and further assuming the hydrogen vapor is in thermal equilibrium with the air a single equation is required to describe the temperature of the condensed hydrogen. This is given by:

$$\rho_{p_{H_2}} \frac{d \epsilon_{p_{H_2}}}{dt} = \dot{Q}_{H_2} - \dot{W}_{v_{H_2}} L_{H_2} \quad (28)$$

where  $\dot{Q}_{H_2}$  is the heat transferred to the particles of hydrogen and  $L_{H_2}$  is the heat of vaporization.

State:

Assuming perfect gas behavior, we have for the total gas phase:

$$\rho_g = \frac{P_o}{RT_g \sum_j Y_j / w_j} \quad (29)$$

Furthermore, the mass concentration of hydrogen vapor at the particle surface is given by:

$$\rho_{gH_2s} = \frac{2 P_{H_2s}}{RT_p} \quad (30)$$

In addition, the phase equilibrium constants are given by:

$$\log_{10} K_{fO_2} = 9.131 - \frac{482}{T_g} - \log_{10} 760 P_0 \quad (31)$$

and

$$\log_{10} K_{fH_2} = 7.659 - \frac{359}{T_g} - \log_{10} 760 P_0$$

Static Enthalpy:

$$\begin{aligned} h_{gO_2} &= 0.215 T_g \\ h_{gH_2} &= 0.246 T_g \\ h_{gH_2} &= \begin{cases} 15 T_g & ; T_g \leq 10^4 K \\ 2.5 T_g + 125 & ; T_g > 10^4 K \end{cases} \end{aligned} \quad (32)$$

and the condensed phase enthalpies are obtained by subtracting appropriate heat of vaporization values for each of the three components.

Rate Relations:

Mass Transfer:

The mass transfer from the particles is taken to be proportional to the difference in mass concentration of hydrogen at the particle surface and in the bulk gas phase. Thus, we have for low Reynolds No. flow about the particle:

$$\dot{W}_{VH_2} = \frac{3 \rho_p X_{H_2} D}{\delta_{H_2} r_p^2} (\rho_{gH_2s} - \rho_{gH_2}) \quad (33)$$

where D is the diffusion coefficient for mass transfer.



Heat Transfer:

The heat transferred to the particle is proportional to the temperature difference. Accounting for the energy given up to the hydrogen vapor flowing away from the particle we have:

$$\dot{Q}_{H_2} = \frac{3 \rho_p X_{H_2} K (T_g - T_p)}{\delta_{H_2} r_p^2} \left\{ \frac{\frac{\dot{w}_v c_{pH_2}}{4\pi r_p h}}{e^{\frac{\dot{w}_v c_{pH_2}}{4\pi r_p h}} - 1} \right\} \quad (34)$$

Summary of Governing Equations:

Continuity of Condensed Hydrogen Mass:

$$\frac{d(1-\bar{z})X_{H_2}}{dt} = \frac{\bar{D}(1-\bar{z})X_{H_2}(\rho_{gH_2} - \rho_{gH_2,s})}{\delta_{H_2} r_p^2} \quad (35)$$

Particle Radius:

$$\frac{dr_p}{dt} = \frac{\bar{D}}{3\delta_{H_2} r_p} (\rho_{gH_2} - \rho_{gH_2,s}) \quad (36)$$

Energy:

Global:

$$\bar{z}(\gamma_{O_2} h_{gO_2} + \gamma_{N_2} h_{gN_2} + \gamma_{H_2} h_{gH_2}) + (1-\bar{z})(X_{O_2} h_{pO_2} + X_{N_2} h_{pN_2} + X_{H_2} h_{pH_2}) = \text{const} \quad (37)$$

Condensed Hydrogen:

$$\frac{d\epsilon_{pH_2}}{dt} = \frac{K(T_g - T_p)}{\delta_{H_2} r_p^2} \left\{ \frac{\frac{\dot{w}_v c_{pH_2}}{4\pi r_p h}}{e^{\frac{\dot{w}_v c_{pH_2}}{4\pi r_p h}} - 1} \right\} + \frac{\bar{D} L_{H_2}}{\delta_{H_2} r_p^2} (\rho_{gH_2} - \rho_{gH_2,s}) \quad (38)$$

Equilibrium Air Relations:

The working form of these relations are given by Eq. 's 21 a, b and 22 a, b.

Summation of Mass Fractions:

These relations for the mass fractions in each phase are given by Eq. 's

23 and 24.

### State Relations:

These are given by Eq. 's 29 through 32.

Note that the governing equations are similar with respect to  $t/r_p^2$  where  $r_{p0}$  is the initial particle radius. The ten unknowns  $r_p$ ,  $X_i$ ,  $Y_i$ ,  $T_g$ ,  $T_p$ , and  $z$  are governed by Eq. 's 35, 36, 37, 38, 21 a,b, 22 a,b, 23 and 24 where the equations of state have been substituted.

The solution of the ten equations was obtained by converting the algebraic integrals to ordinary differential equations. This system was integrated simultaneously by a standard predictor-corrector package after inverting the coefficient matrix by Gaussian reduction. The general form of the governing differential equations is given by:

$$\sum_j B_{ij} \dot{Q}_j = F_i \quad (39)$$

where the  $B_{ij}$  and the  $F_i$  are functions of the  $Q_j$ 's and are given in Appendix I.

The initial conditions, i.e., the initial  $Q_j$ 's, are fixed by specifying  $T_p$ ,  $r_{p0}$ ,  $T_g$ ,  $B_i$ ,  $P_0$  and the arbitrary amount of  $B_{H_2}$  which is in the condensed phase. The initial  $T_g$ ,  $B_i$ ,  $P_0$  and the condensed fraction of hydrogen together with Eq. 's 21 through 24 fix the distribution of the air between the two phases. Thus, the  $X_i$ ,  $Y_i$  and  $z$  are determined at the initial point.

The pertinent thermodynamic data were obtained from References 2, 3, 4, 5, and 6 and the transport coefficients were computed from work presented in Reference 7.

### III DISCUSSION:

The results of the calculations are shown in the attached curves. Each set of curves, a through d, display the time history of the variables in question under a particular set of initial conditions. Figures a show the particle radius,  $r$ , and ratio of total gas phase mass to the mass,  $z$ . Figures b show the hydrogen particle temperature and the gas phase temperature. Figures c and d show the gas phase and condensed phase mass fractions, respectively.

We see that for all cases considered the evaporation time is of the order of  $10^{-5}$  seconds for 1 micron particles. Case by case, however, the evaporation histories are substantially different, that is, the occurrence of two-phase air during the evaporation process is a feature of considerable interest regarding general behavior of two-phase flow problems. For example, in Figures 1, 2 and 3, the conditions are such that the air is initially all in the gas phase. The subsequent cooling of the air is sufficient to bring it into the two-phase region. The criteria for establishing the point at which the air begins to condense is determined by satisfying the equilibrium relations under the condition that the air is all gas. That is, by considering  $O_2$ , say, as all gaseous, a relation fixing the saturation point of the air subsystem may be derived. This is given in Appendix II. The results shown in Figure 4 are based on conditions for which two-phase air exists

initially. This can be seen in Figures 4c and d. An interesting feature of this case is the behavior of the particle temperature which passes through a minimum before reaching the point of complete hydrogen evaporation. The reason is associated with the energy the particle loses by evaporation relative to energy externally applied to the particle. Thus, for the case under consideration the heat reaching the particle is insufficient for evaporation and the additional energy must be derived from the particle itself. Thus, the particle energy decreases which is accompanied by the temperature decrease. Since, however, the heat transferred to the particle increases faster than the evaporation rate during the evaporation process a minimum temperature is reached and a reversal in this trend occurs. Figure 5 shows the effect of an initial air temperature sufficiently high so that no air condensation occurs during the evaporation process. In this case, the larger temperature difference is such that the heat transferred to the particle is sufficient to supply the heat of vaporization and, in addition, to raise the particle temperature, Figure 5b. The effect of variable particle temperature is shown in Figure 6. Here, the same initial conditions as those applied in obtaining the results in Figure 5 were used with the exception that the particle temperature was held constant. The time for evaporation increases by a factor of five (5) which illustrates the importance of properly accounting for particle temperature variation. Note that in cases where the particle temperature normally would decrease, the constant

temperature assumption would tend to decrease the evaporation time.

Figure 7 shows the results of calculations for the evaporation of condensed hydrogen in an atmosphere of hydrogen gas. In Figure 8 a constant particle temperature calculation is presented having the same initial conditions used in computing the results shown in Figure 7. These hydrogen into hydrogen cases are not of particular importance in the present context and are presented for comparative purposes only. A further point of interest is the effect of heating the hydrogen vapor as it passes from the particle surface temperature to the surrounding gas temperature. This effect is accounted for in the bracketed quantity of the first term on the right hand side of Eq. 34. If this quantity is allowed to equal unity then, in effect, all the energy transferred through the film reaches the particle. Figure 34 contains the results of this assumption for the same initial conditions used in arriving at the results in Figure 2. Although the effect is not extensive there is a slight increase in particle temperature and subsequent small decrease in evaporation time.

It should be noted that this work is applicable to a streamline calculation provided the acceleration is small. Thus, the present analysis may be applied for the determination of variable outer edge conditions in a fairly important class of two-phase boundary layer problems.

In general, the resulting evaporation times are strongly dependent on the continuum assumption regarding the behavior of the vaporsurrounding the condensed particles. When high altitudes are encountered, say above 40 km, with particles of the order of 1 to 10 microns, it may be necessary to revise the analysis to account for the effect of having rarefied air relative to the particles.

LIST OF SYMBOLS

$B_i$  = mass fraction of species  $i$  in the total mixture.

$C_p$  = specific heat cal/gm  $^{\circ}K$

$\bar{D} = 3D$ ;  $D$  = particle diffusion coefficient  $\frac{cm^2}{sec}$

$e_p$  = particle internal energy  $\frac{cal}{gm}$

$h$  = enthalpy -  $\frac{cal}{gm}$

$K_f$  = phase equilibrium constant

$\bar{K} = 3K$ ;  $K$  = particle thermal conductivity coefficient  $\frac{cal}{^{\circ}K-cm-sec}$

$I_{H_2}$  = heat of vaporization  $\frac{cal}{gm}$

$P$  = Pressure atm

$\dot{Q}$  = Heat transfer rate  $\frac{cal}{cm^2-sec}$

$R$  = gas constant per mole

$r_p$  = particle radius - cm

$T$  = absolute temperature  $^{\circ}K$

$t$  = time sec

$W$  = molecular weight

$W_{gg} = \left( \sum_i \frac{Y_i}{W_i} \right)^{-1}$  = gas phase molecular weight

$W_{pp} = \left( \sum_i \frac{X_i}{W_i} \right)^{-1}$  = condensed phase molecular weight

$\dot{W}_v$  = evaporation rate  $\frac{\text{gm}}{\text{cm}^3 \cdot \text{sec}}$

$X_i, \overline{X_i}$  = mass and mole fraction respectively of  $i$ th condensed species in total condensed phase

$Y_i, \overline{Y_i}$  = mass and mole fraction respectively of  $i$ th gaseous species in total gaseous phase

$\overline{X_i}'$  = mole fraction of  $i$ th condensed species in total air condensed phase

$\overline{Y_i}'$  = mole fraction of  $i$ th gaseous species in total air gaseous phase

$\beta$  = ratio of total gas phase mass to total mixture mass

$\rho_{gH_2}$  = mass concentration of gas phase hydrogen

$\rho_{gH_2s}$  = mass concentration of gas phase hydrogen at particle surface

$\delta_{H_2}$  = condensed particle density

$\mu_i$  = gibbs potential



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## APPENDIX I

APPENDIX I

The terms appearing in eq. 's 13 are given in the following:

The  $Q_j$ 's are defined as follows:

$$Q_1 = \dot{\gamma}$$

$$Q_2 = X_{O_2}$$

$$Q_3 = X_{N_2}$$

$$Q_4 = X_{H_2}$$

$$Q_5 = Y_{O_2}$$

$$Q_6 = Y_{N_2}$$

$$Q_7 = Y_{H_2}$$

$$Q_8 = T_g$$

$$Q_9 = T_p$$

$$Q_{10} = r_p$$

AI-1

where the total time derivative is determined by:

$$\dot{Q}_j = \frac{dQ_j}{dt}$$

AI-2

The  $B_{ij}$ 's are the coefficients of the  $Q_j$ 's and each  $B_{ij}$  is associated with a particular governing equation as listed below:

|                          | Equation         |
|--------------------------|------------------|
| $B_{1j} \longrightarrow$ | 1                |
| $B_{2j}$                 | 6a for $i = O_2$ |
| $B_{3j}$                 | 6b for $i = N_2$ |
| $B_{4j}$                 | 8                |

AI-3

|           |                   |                  |
|-----------|-------------------|------------------|
| $B_{5j}$  | $\longrightarrow$ | 5a for $i = O_2$ |
| $B_{6j}$  |                   | 5b for $i = N_2$ |
| $B_{7j}$  |                   | 7                |
| $B_{8j}$  |                   | 4                |
| $B_{9j}$  |                   | 3                |
| $B_{10j}$ |                   | 2                |

Thus, the  $B_{ij}$ 's are given as follows:

$$B_{11} = -X_{H_2}$$

$$B_{12} = 0$$

$$B_{13} = 0$$

$$B_{14} = 1-2$$

$$B_{15} = 0$$

$$B_{16} = 0$$

$$B_{17} = 0$$

$$B_{18} = 0$$

$$B_{19} = 0$$

$$B_{1,10} = 0$$

$$B_{21} = \frac{B_{02} \left( \frac{w_{gg}}{w_{pp}} \right)^2 \left[ \frac{w_{pp}}{w_{gg}} K_{fO_2} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) - \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right)^2 \right]}{\left[ (1-\beta) \frac{w_{gg}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

$$B_{22} = 1 - \frac{B_{02} \beta K_{fO_2} \frac{w_{gg}}{w_{O_2}}}{\left[ (1-\beta) \frac{w_{gg}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

$$B_{23} = \left[ B_{22} - 1 \right] \frac{w_{O_2}}{w_{N_2}}$$

$$B_{24} = 0$$

$$B_{25} = \frac{B_{02} \beta \frac{w_{gg}}{w_{O_2} w_{pp}} K_{fO_2} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right)}{\left[ (1-\beta) \frac{w_{gg}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

AI-5

$$B_{26} = B_{25} \frac{w_{O_2}}{w_{N_2}}$$

$$B_{27} = B_{25} \frac{w_{O_2}}{w_{H_2}}$$

$$B_{28} = \frac{B_{02} \beta \frac{w_{gg}}{w_{pp}} \frac{dK_{fO_2}}{dT_g} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right)}{\left[ (1-\beta) \frac{w_{gg}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

$$B_{29} = 0$$

$$B_{2,10} = 0$$

$$B_{31} = \frac{B_{N_2} \left( \frac{W_{g2}}{W_{PP}} \right)^2 \left[ \frac{W_{PP}}{W_{g2}} K_{fN_2} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) - \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right)^2 \right]}{\left[ (1-\beta) \frac{W_{g2}}{W_{PP}} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

$$B_{32} = \frac{-B_{N_2} \beta \frac{W_{g2}}{W_{O_2}} K_{fO_2}}{\left[ (1-\beta) \frac{W_{g2}}{W_{PP}} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) + \beta K_{fO_2} \right]^2}$$

$$B_{33} = 1 + B_{32} \frac{W_{O_2}}{W_{N_2}}$$

$$B_{34} = 0$$

$$B_{35} = \frac{B_{N_2} \beta \frac{W_{g2}}{W_{O_2} W_{PP}} K_{fN_2} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right)}{\left[ (1-\beta) \frac{W_{g2}}{W_{PP}} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) + \beta K_{fN_2} \right]^2}$$

$$B_{36} = B_{35} \frac{W_{O_2}}{W_{N_2}}$$

AI-6

$$B_{37} = B_{35} \frac{W_{O_2}}{W_{H_2}}$$

$$B_{38} = \frac{B_{N_2} \beta \frac{W_{g2}}{W_{PP}} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) \frac{d K_{fN_2}}{d T_g}}{\left[ (1-\beta) \frac{W_{g2}}{W_{PP}} \left( 1 - X_{H_2} \frac{W_{PP}}{W_{H_2}} \right) + \beta K_{fN_2} \right]^2}$$

$$B_{39} = 0$$

$$B_{3.10} = 0$$

$$B_{41} = 0$$

$$B_{42} = 1$$

$$B_{43} = 1$$

$$B_{44} = 1$$

$$B_{45} = 0$$

$$B_{46} = 0$$

$$B_{47} = 0$$

$$B_{48} = 0$$

$$B_{49} = 0$$

$$B_{4.10} = 0$$

$$B_{51} = \frac{B_{02} K_{502} \frac{w_{g2}}{w_{pp}} \left[ X_{H_2} \frac{w_{pp}}{w_{H_2}} - 1 + \frac{w_{pp}}{w_{g2}} K_{502} \right]}{1}$$

$$B_{52} = \frac{B_{02} K_{502} (1-\beta) \frac{w_{g2}}{w_{02}}}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{502} \right]^2}$$

$$B_{53} = B_{52} \frac{w_{02}}{w_{N_2}}$$

$$B_{54} = 0$$

$$B_{55} = 1 - \frac{B_{02} K_{502} \frac{w_{g2}}{w_{pp} w_{02}} \left[ \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) (1-\beta) \right]}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{502} \right]^2}$$

AI-8

$$B_{56} = [B_{55} - 1] \frac{w_{02}}{w_{N_2}}$$

$$B_{57} = [B_{55} - 1] \frac{w_{02}}{w_{H_2}}$$

$$B_{58} = \frac{-B_{02} \frac{w_{g2}}{w_{pp}} \frac{dK_{502}}{dT_g} \left[ \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) (1-\beta) \right]}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} \left( 1 - X_{H_2} \frac{w_{pp}}{w_{H_2}} \right) + \beta K_{502} \right]}$$

$$B_{59} = 0$$

$$B_{5.10} = 0$$



$$B_{61} = \frac{B_{N_2} K_{FN_2} \frac{w_{g2}}{w_{pp}} \left[ X_{H_2} \frac{w_{pp}}{w_{H_2}} - 1 + \frac{w_{pp}}{w_{g2}} K_{FN_2} \right]}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) + \beta K_{FN_2} \right]^2}$$

$$B_{62} = \frac{B_{N_2} K_{FN_2} (1-\beta) \frac{w_{g2}}{w_{o2}}}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) + \beta K_{FN_2} \right]^2}$$

$$B_{63} = B_{62} \frac{w_{o2}}{w_{N_2}}$$

$$B_{64} = 0$$

$$B_{65} = [B_{66} - 1] \frac{w_{N_2}}{w_{o2}}$$

AI-9

$$B_{66} = 1 - \frac{B_{N_2} K_{FN_2} \frac{w_{g2}^2}{w_{pp} w_{N_2}} \left[ (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) (1-\beta) \right]}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) + \beta K_{FN_2} \right]^2}$$

$$B_{67} = [B_{66} - 1] \frac{w_{N_2}}{w_{H_2}}$$

$$B_{68} = \frac{- B_{N_2} \frac{w_{g2}}{w_{pp}} \frac{d K_{FN_2}}{dT_2} \left[ (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) (1-\beta) \right]}{\left[ (1-\beta) \frac{w_{g2}}{w_{pp}} (1 - X_{H_2} \frac{w_{pp}}{w_{H_2}}) + \beta K_{FN_2} \right]^2}$$

$$B_{69} = 0$$

$$B_{6.10} = 0$$

$$B_{71} = 0 \quad B_{76} = 1$$

$$B_{72} = 0 \quad B_{77} = 1$$

$$B_{73} = 0 \quad B_{78} = 0$$

$$B_{74} = 0 \quad B_{79} = 0$$

$$B_{75} = 1 \quad B_{7.10} = 0$$

AI-10

$$B_{81} = (Y_{O_2} h_{gO_2} + Y_{N_2} h_{gN_2} + Y_{H_2} h_{gH_2}) - (X_{O_2} h_{pO_2} + X_{N_2} h_{pN_2} + X_{H_2} h_{pH_2})$$

$$B_{82} = (1-z) h_{pO_2}$$

$$B_{83} = (1-z) h_{pN_2}$$

$$B_{84} = (1-z) h_{pH_2}$$

$$B_{85} = z h_{gO_2}$$

$$B_{86} = z h_{gN_2}$$

$$B_{87} = z h_{gH_2}$$

$$B_{88} = z \left[ Y_{O_2} \frac{dh_{gO_2}}{dT_g} + Y_{N_2} \frac{dh_{gN_2}}{dT_g} + Y_{H_2} \frac{dh_{gH_2}}{dT_g} \right] + (1-z) \left[ X_{O_2} \frac{dh_{pO_2}}{dT_g} + X_{N_2} \frac{dh_{pN_2}}{dT_g} \right]$$

$$B_{89} = (1-z) X_{H_2} \frac{dh_{pH_2}}{dT_g}$$

$$B_{8.10} = 0$$

AI-11

$$B_{91} = 0$$

$$B_{10.1} = 0$$

$$B_{92} = 0$$

$$B_{10.2} = 0$$

$$B_{93} = 0$$

$$B_{10.3} = 0$$

$$B_{94} = 0$$

$$B_{10.4} = 0$$

$$B_{95} = 0$$

AI-12

$$B_{10.5} = 0$$

AI-13

$$B_{96} = 0$$

$$B_{10.6} = 0$$

$$B_{97} = 0$$

$$B_{10.7} = 0$$

$$B_{98} = 0$$

$$B_{10.8} = 0$$

$$B_{99} = C_{V_{H_2}}$$

$$B_{10.9} = r_p^2 \frac{d\delta_{H_2}}{dT_p}$$

$$B_{0.10} = 0$$

$$B_{10.10} = 3r_p \delta_{H_2}$$

### Forcing Functions

$$F_1 = \frac{\bar{D}(1-\beta)X_{H_2}}{\delta_{H_2} r_p^2} [g_{H_2} - g_{H_2s}]$$

$$F_2 = 0$$

$$F_7 = 0$$

$$F_3 = 0$$

$$F_8 = 0$$

$$F_4 = 0$$

$$F_9 = \bar{K}(T_g - T_p) \left\{ \frac{\frac{(\dot{W}_r C_p)_{H_2}}{4\pi r_p \pi_f}}{\frac{(\dot{W}_r C_p)_{H_2}}{4\pi r_p \pi_f} - 1} \right\} + \frac{\bar{D}L_{H_2}}{\delta_{H_2} r_p^2} (g_{H_2} - g_{H_2s}) e^{\frac{(\dot{W}_r C_p)_{H_2}}{4\pi r_p \pi_f} - 1}$$

$$F_5 = 0$$

$$F_{10} = \bar{D}(g_{H_2} - g_{H_2s})$$

$$F_6 = 0$$

## APPENDIX II

In the present "partial" equilibrium analysis equations 5a, b, and 6a, b express relations between the mass (or mole) fractions within the equilibrium subsystem of the overall mixture. We shall discuss briefly here the development of these relations for an ideal mixture.

In terms of mole fractions the Gibbs potentials are given by:

condensed phase:

$$\bar{\mu}_{ic} = \bar{g}_{ic} + \bar{R}T \ln \bar{x}_i \quad \text{A II-1}$$

where

$$\bar{g}_{ic} = \bar{\mu}_{ic}^0 + \bar{R}T \ln P_i^s \quad \text{A II-2}$$

therefore,

$$\bar{\mu}_{ic} = \bar{\mu}_{ic}^0 + \bar{R}T \ln \bar{x}_i P_i^s \quad \text{A II-3}$$

and similarly for the gas phase:

$$\bar{\mu}_{ig} = \bar{\mu}_{ig}^0 + \bar{R}T \ln \bar{y}_i P_g^s \quad \text{A II-4}$$

where it is understood that the fugacities are identical to the pressures and the activity coefficient are unity. Furthermore, the mixing process which defines Eq.'s AII-3 and AII-4 is one in which the pure condensed phase components are under their vapor pressures and the pure gas phase components are each under the mixture pressure.

Now the equilibrium condition requires the potential of each species to be equal in each phase. Thus, we have:

$$\bar{\mu}_{ic} = \bar{\mu}_{ig} \quad \text{A II-5}$$

it follows that:

$$\bar{X}_i' P_{i,s} = \bar{Y}_i' P_g' \quad \text{A II-6}$$

or

$$\frac{\bar{Y}_i'}{\bar{X}_i'} = \frac{P_{i,s}}{P_g'} \equiv K_{fi} \quad \text{A II-7}$$

Note that the primed variables refer to the equilibrium subsystem and therefore i applies to  $O_2$  and  $N_2$ .

The net conservation of global mass may be written:

$$\beta_j = z_j \bar{Y}_j' + (1-z_j) \bar{X}_j \quad j = O_2, N_2, H_2 \quad \text{A II-8}$$

and upon applying this general statement to  $O_2$  and  $N_2$ , we get

Eq.'s 5a, b and 6a, b.

Criteria for establishing state at which air enters two-phase region:

We have:

$$\bar{Y}_{O_2}' = \bar{X}_{O_2}' K_{fO_2} = \frac{\bar{X}_{O_2}}{1 - \bar{X}_{H_2}} K_{fO_2} \quad (1)$$

and

$$\bar{Y}_{N_2}' = \bar{X}_{N_2}' K_{fN_2} = \frac{\bar{X}_{N_2}}{1 - \bar{X}_{H_2}} K_{fN_2} \quad (2)$$

but

(3)

We have: Equation 1.

$$\bar{Y}_{O_2} = \frac{\bar{X}_{O_2} K_{fO_2}}{1 - \bar{X}_{H_2}} \quad (5)$$

and with equations 3 and 4, equation 2 becomes:

$$1 - \bar{Y}_{O_2} - \bar{Y}_{H_2} = \left[ \frac{1 - \bar{X}_{O_2} - \bar{X}_{H_2}}{1 - \bar{X}_{H_2}} \right] K_{fN_2} \quad (6)$$

Combining (5) and (6), we get:

$$\bar{Y}_{O_2} = \left[ (K_{fN_2} - 1) + \bar{Y}_{H_2} \right] \frac{K_{fO_2}}{K_{fN_2} - K_{fO_2}} \quad (7)$$

but

$$\bar{Y}_{O_2} = \bar{Y}_{O_2}' (1 - \bar{Y}_{H_2})$$

(Note prime denotes air subsystem.)

and  $\bar{Y}_{O_2}'$  is constant until condensation of air occurs.

$$\text{Thus } \bar{Y}_{O_2}' = 0.21$$

$\therefore$  (7) may be written

$$\left[ (K_{fN_2} - 1) + \bar{Y}_{H_2} \right] \frac{K_{fO_2}}{(K_{fN_2} - K_{fO_2})(1 - \bar{Y}_{H_2})} = 0.21 \quad (8)$$

Also,

$$\bar{X}_{O_2} = (1 - \bar{X}_{H_2}) \left[ \frac{(K_{fN_2} - 1) + \bar{Y}_{H_2}}{K_{fN_2} - K_{fO_2}} \right] \quad (9)$$

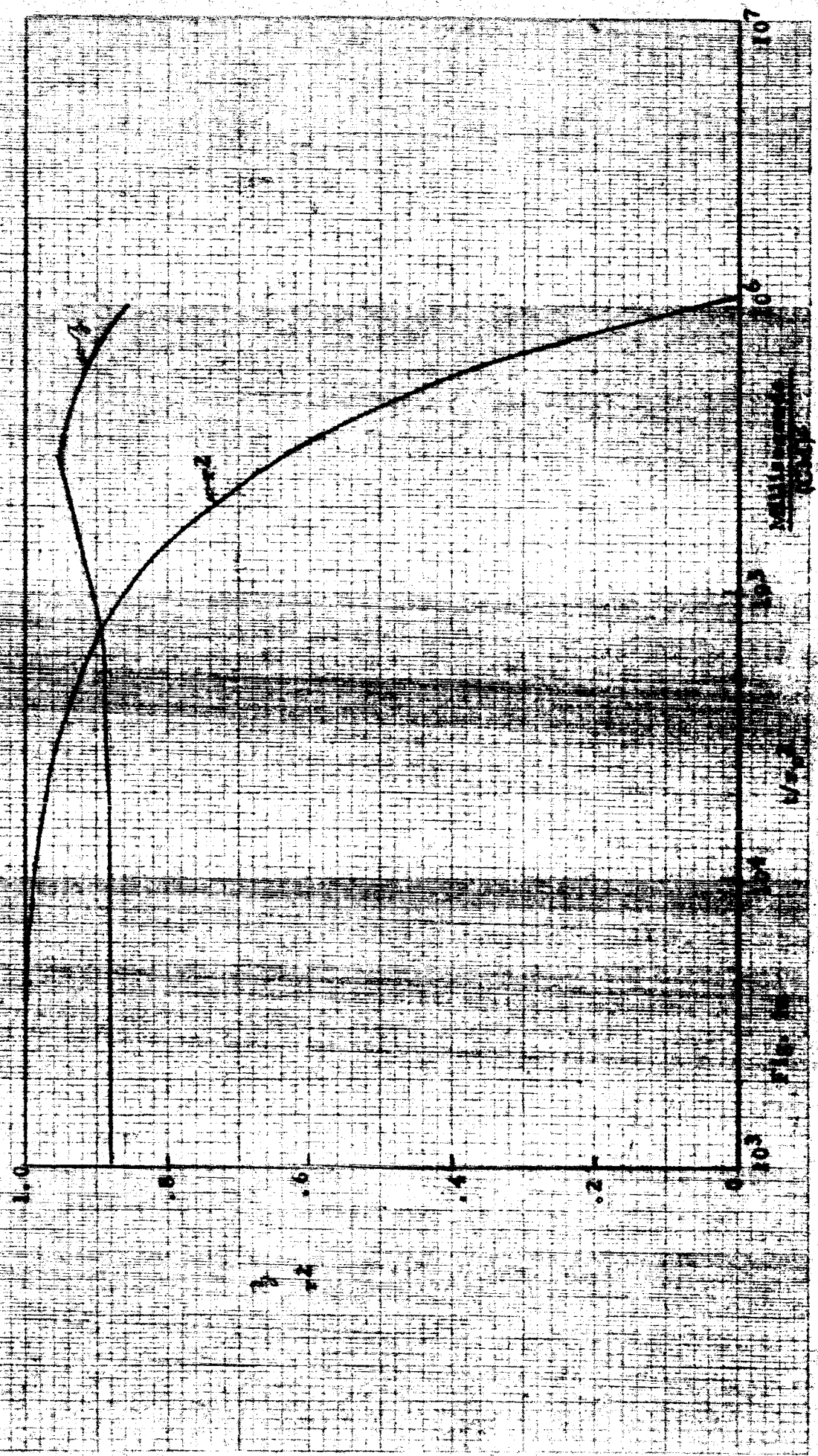
Eq. (9) is not needed here.

Now, Eq. (8) is satisfied at a particular state and represents the point at which condensation begins. That is, it satisfies equilibrium at a state where all  $O_2$  is gas, i.e.  $\bar{Y}_{O_2}' = 0.21$ .

| Figure | P <sub>o</sub><br>ATM | z       | T <sub>g</sub><br>°K | T <sub>p</sub><br>°K | BO <sub>2</sub> | BN <sub>2</sub> | BH <sub>2</sub> | BO <sub>2</sub> <sup>s</sup> | BN <sub>2</sub> <sup>s</sup> | BH <sub>2</sub> <sup>s</sup> |
|--------|-----------------------|---------|----------------------|----------------------|-----------------|-----------------|-----------------|------------------------------|------------------------------|------------------------------|
| 1      | 0.054                 | 0.8782  | 150                  | 10                   | 0.2046          | 0.6736          | 0.1218          | 0                            | 0                            | 0.1218                       |
| 2      | 0.054                 | 0.6164  | 300                  | 10                   | 0.1430          | 0.4734          | 0.3836          | 0                            | 0                            | 0.3836                       |
| 3      | 0.054                 | .8782   | 150                  | 10                   | 0.2046          | 0.6736          | 0.1218          | 0                            | 0                            | 0.1218                       |
| 4      | 0.6728                | 0.34131 | 70                   | 25                   | 0.1986          | 0.6537          | 0.1478          | 0.1777                       | 0.3628                       | 0.1200                       |
| 5      | 0.054                 | 0.866   | 300                  | 10                   | 0.155           | 0.510           | 0.335           | 0                            | 0                            | 0.118                        |
| 6      | 0.054                 | 0.866   | 300                  | 10                   | 0.155           | 0.510           | 0.335           | 0                            | 0                            | 0.118                        |
| 7      | 0.054                 | 0.600   | 300                  | 10                   | 0               | 0               | 1.0             | 0                            | 0                            | 0.40                         |
| 8      | 0.054                 | 0.600   | 300                  | 10                   | 0               | 0               | 1.0             | 0                            | 0                            | 0.40                         |



Particle Radius and Degree of Vaporization vs  $t/\tau_0^2$



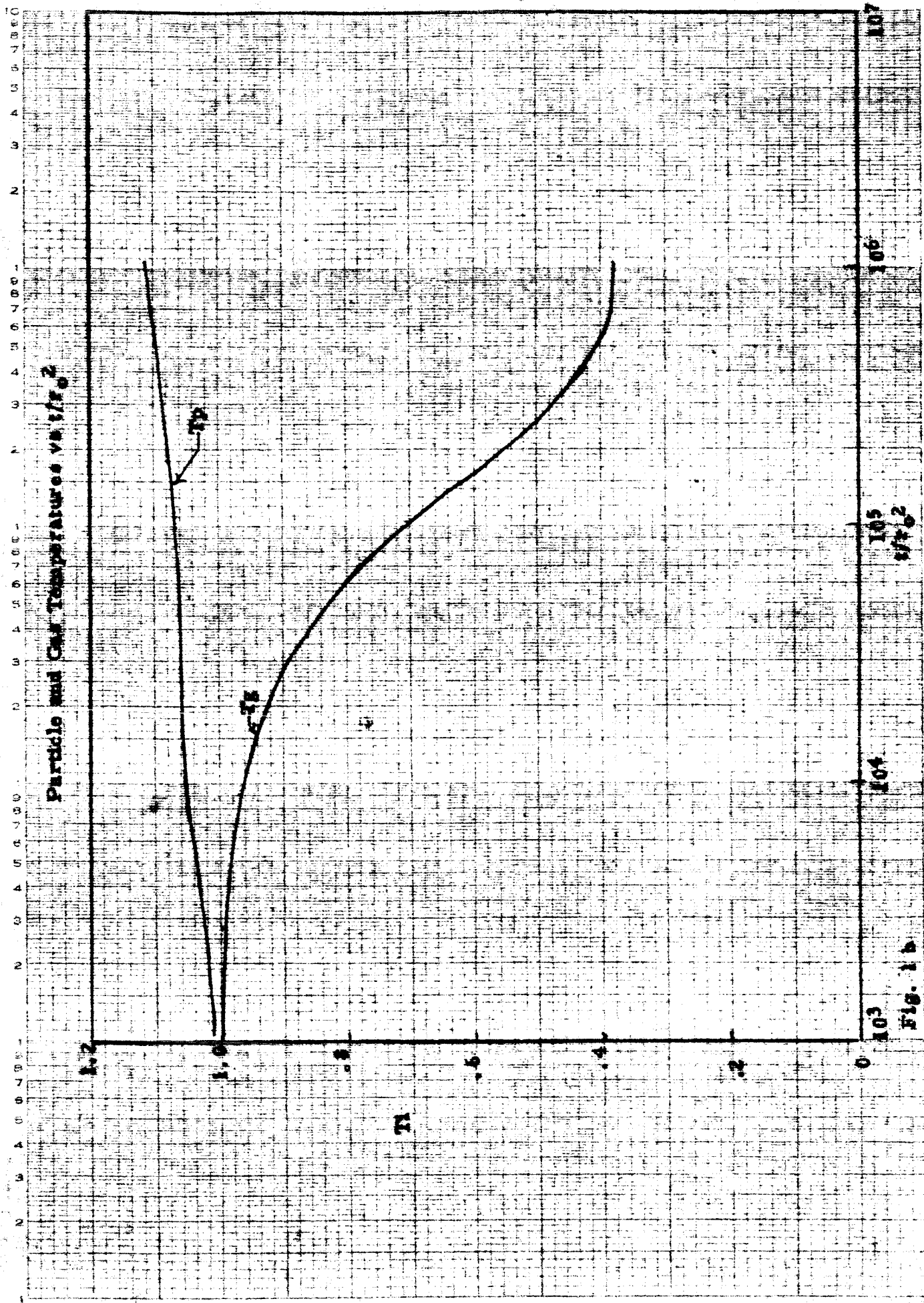


Fig. 1 b

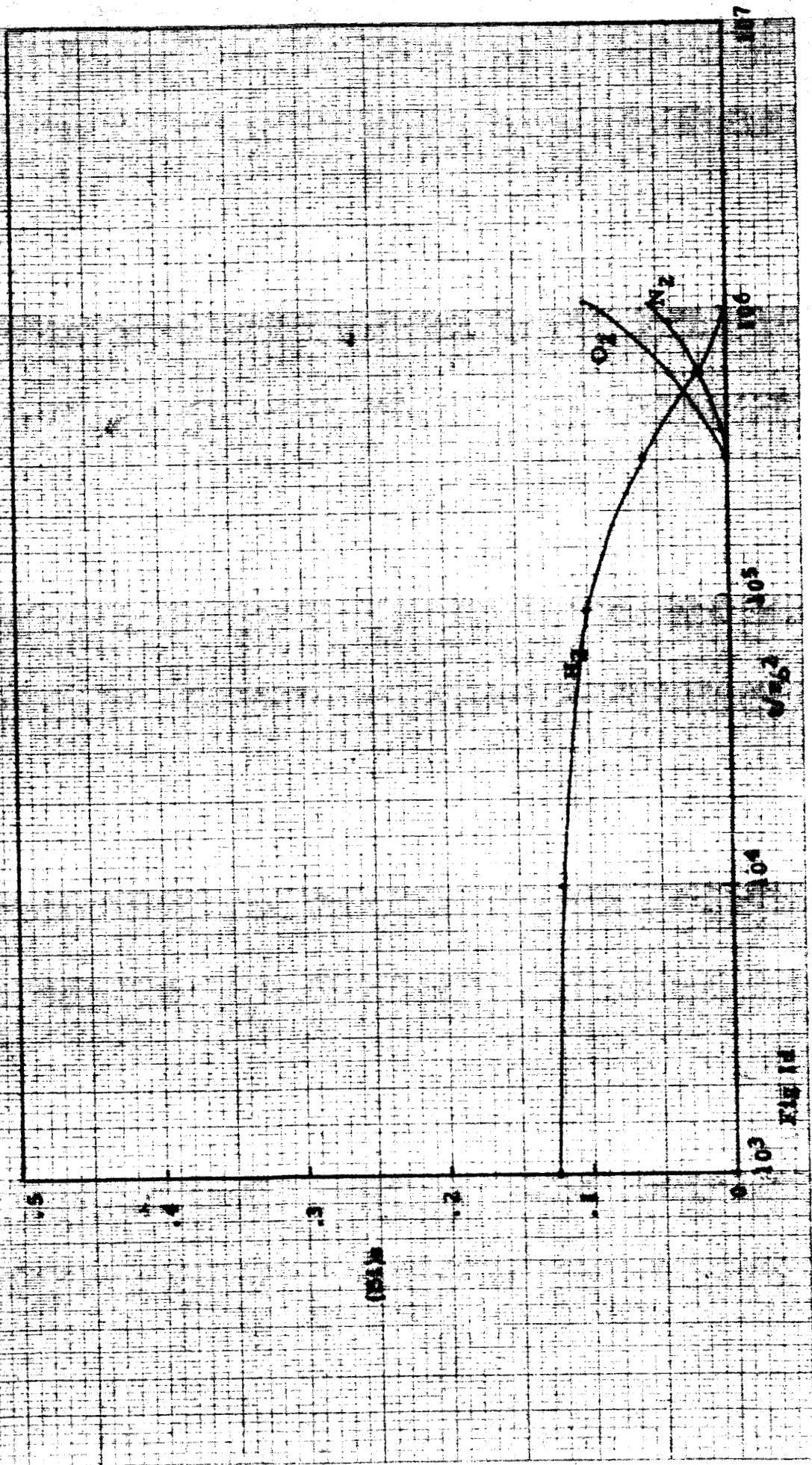
Can Phase Mass Fractions via  $t/\tau_{0.3}$



FIG 1c



Condensed Phase Mass Fractions vs  $t/\tau_0^2$



Particle Radius and Degree of Vaporization vs  $t/\tau_0^2$

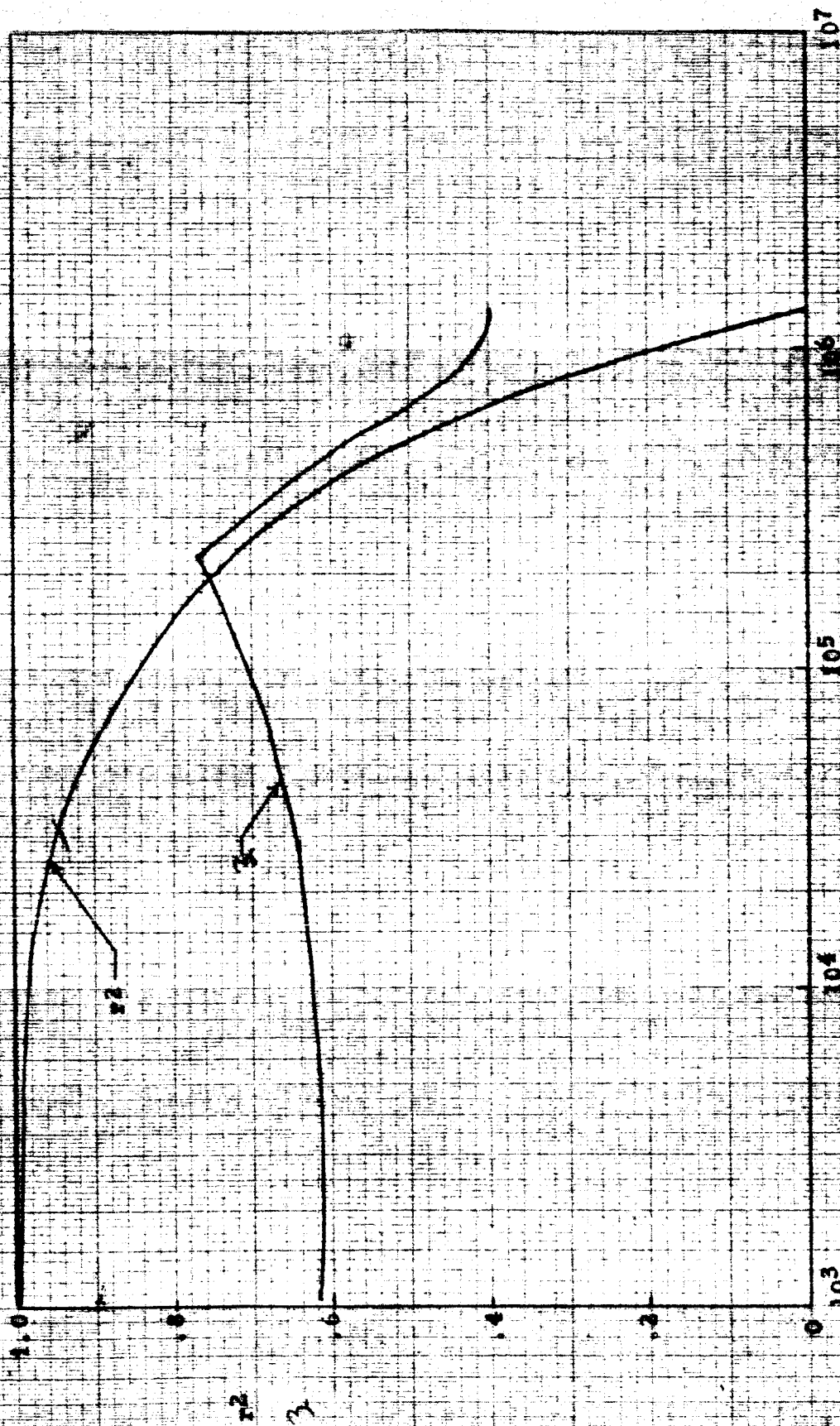


Fig 2a  $t/\tau_0^2$

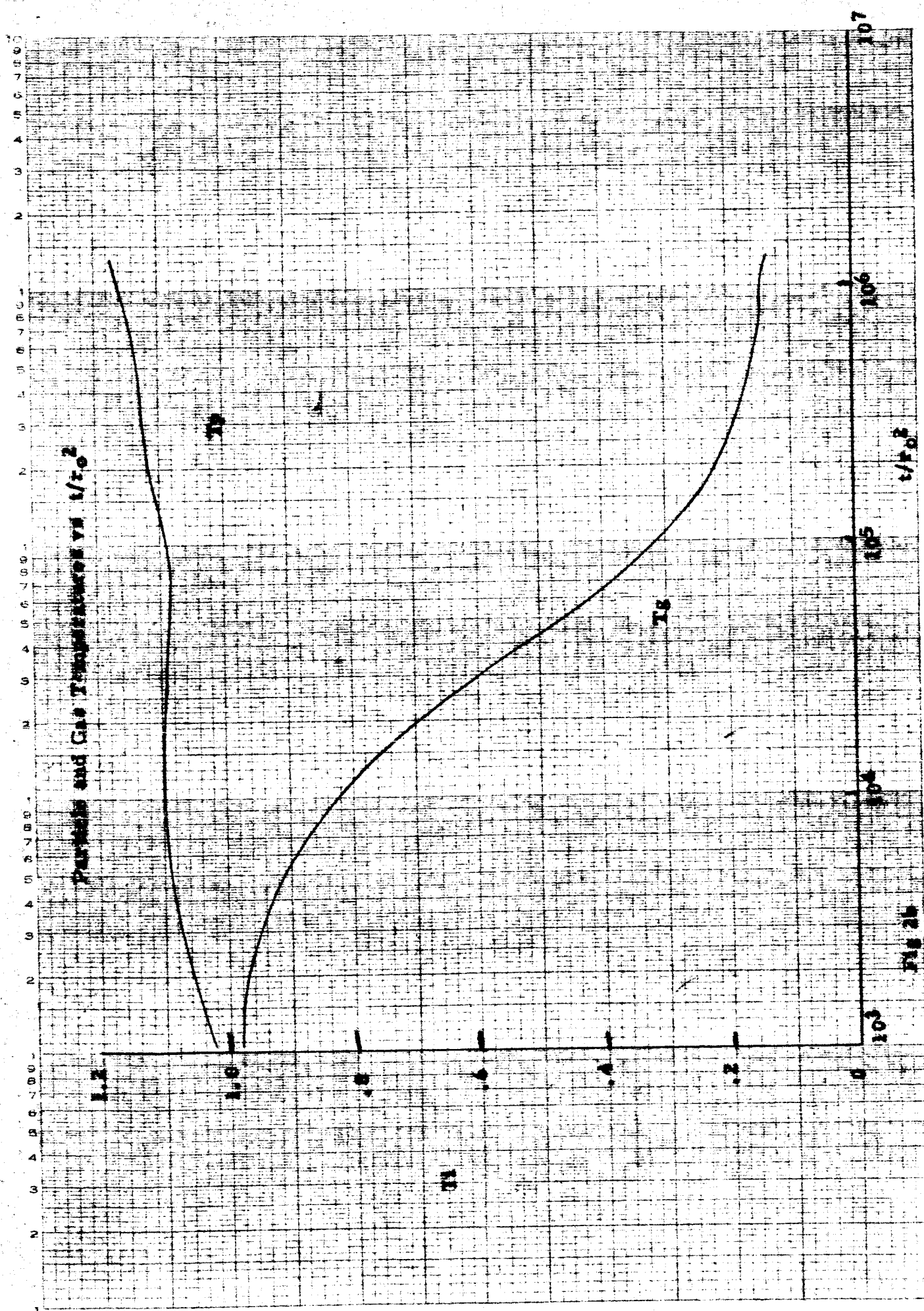


Fig 2b



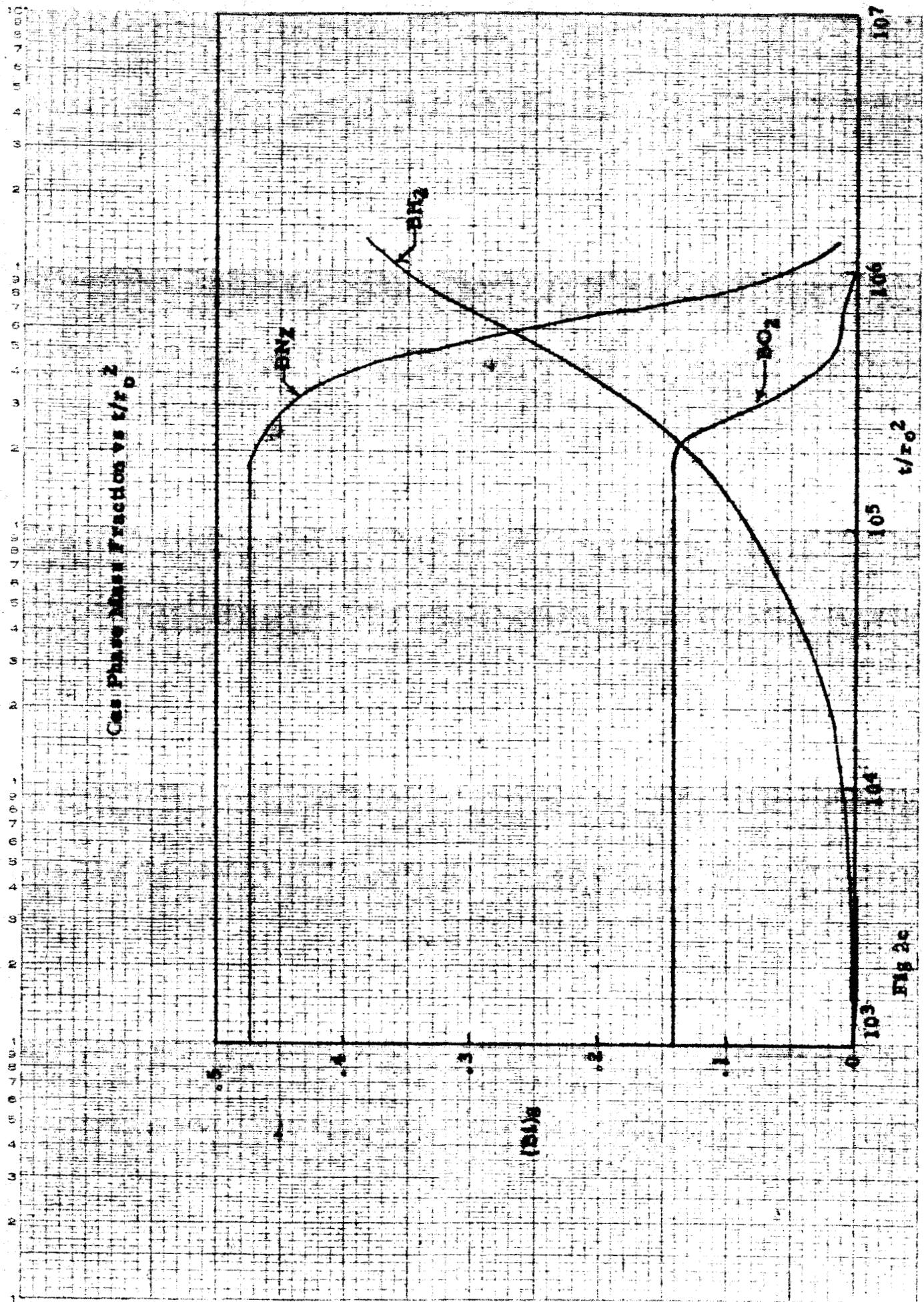
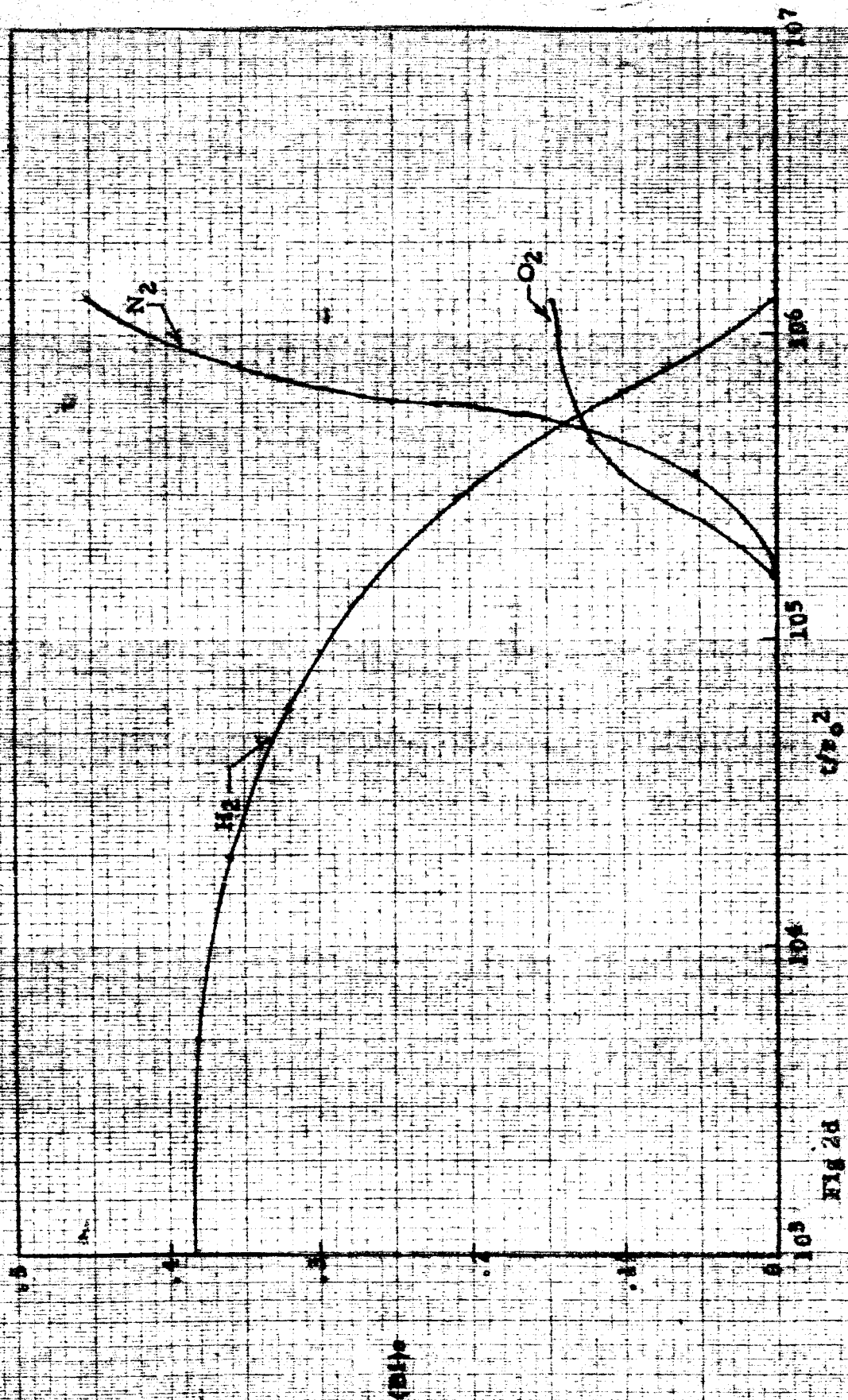


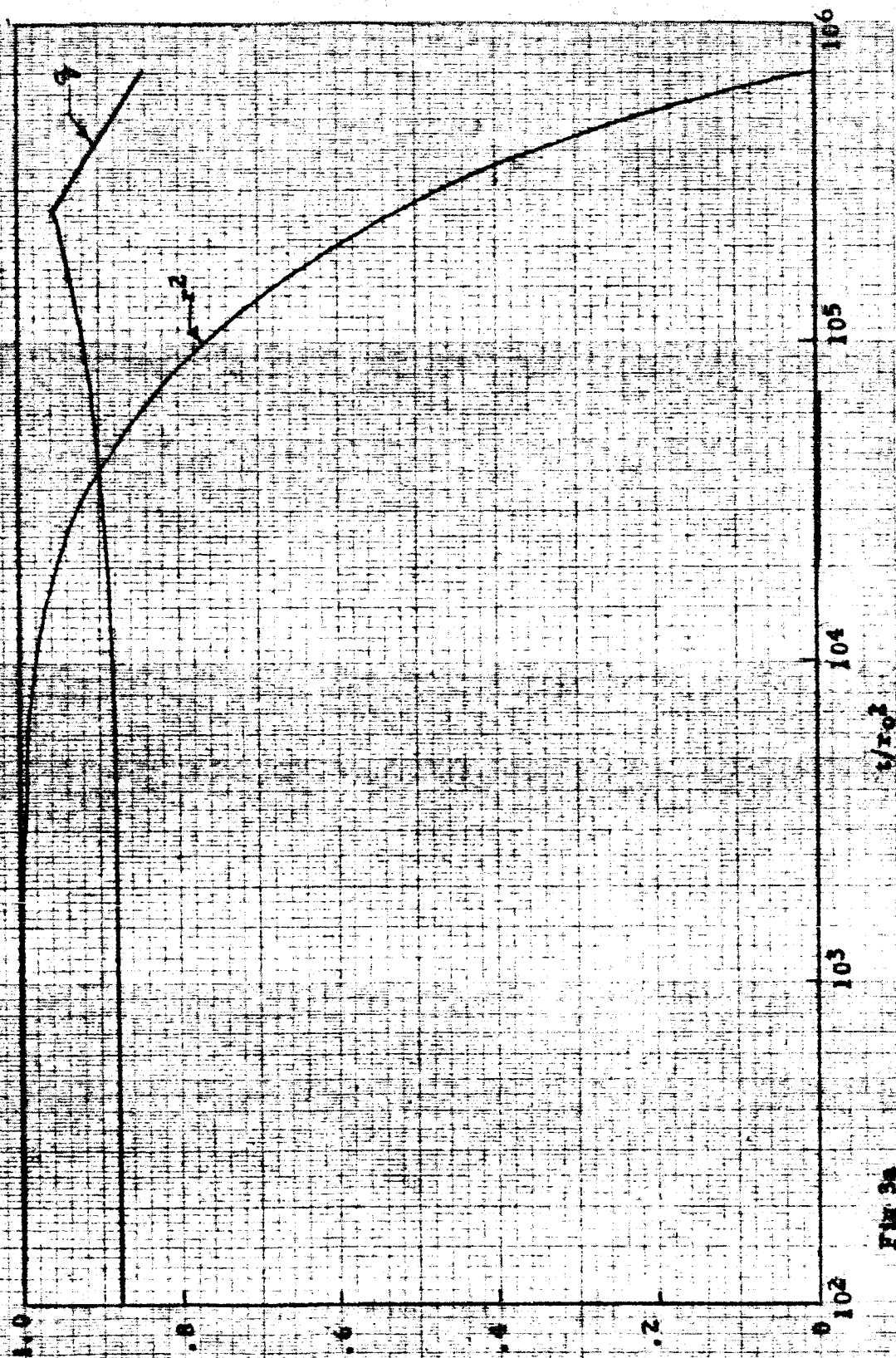
Fig 2c

Condensed Phase Mass Fractions vs  $p/p_0$





Particle Radius and Degree of Vaporization vs  $r_0^2$



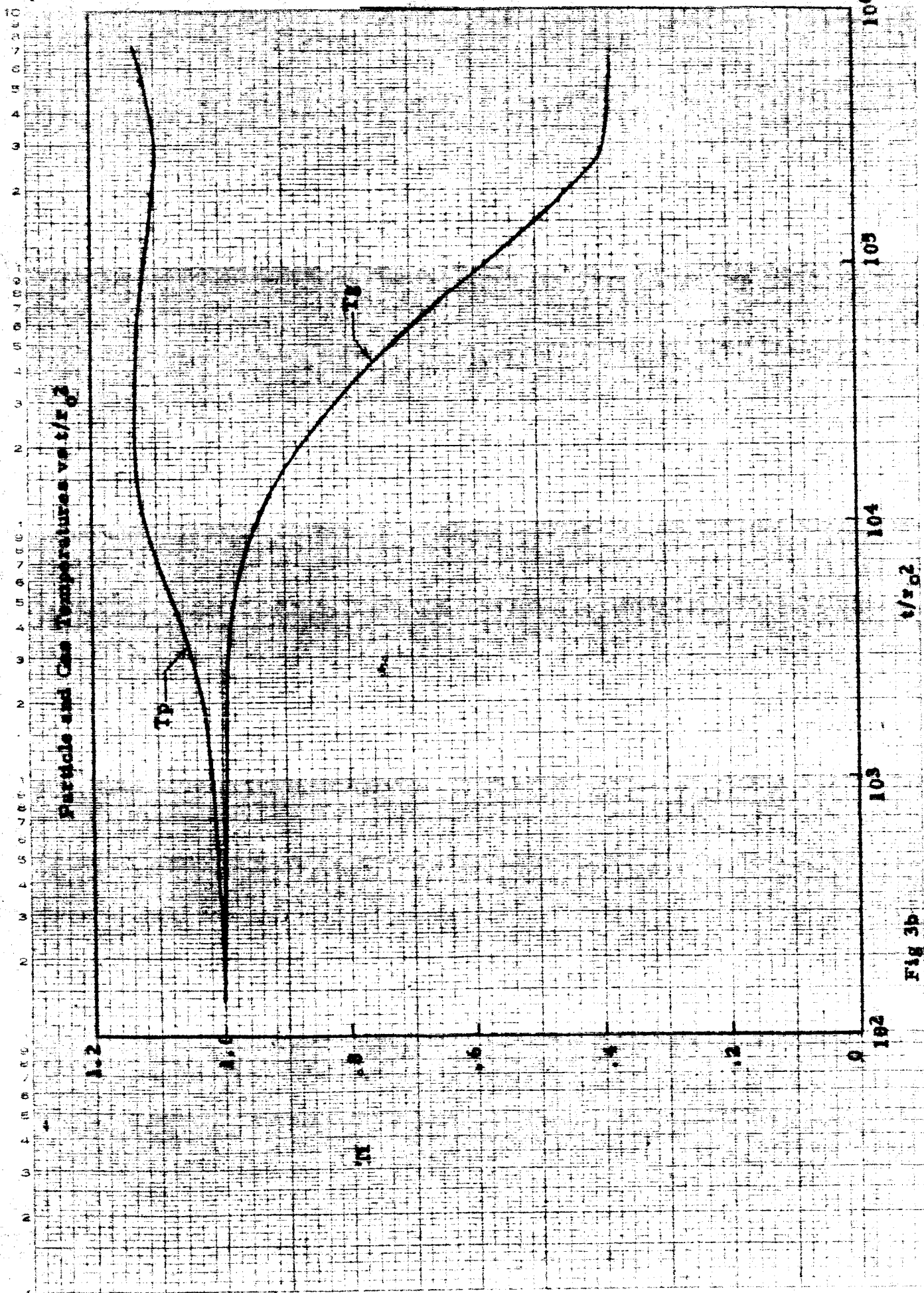


Fig 3b

Gas Phase Mass Fractions vs  $t/r_0^2$

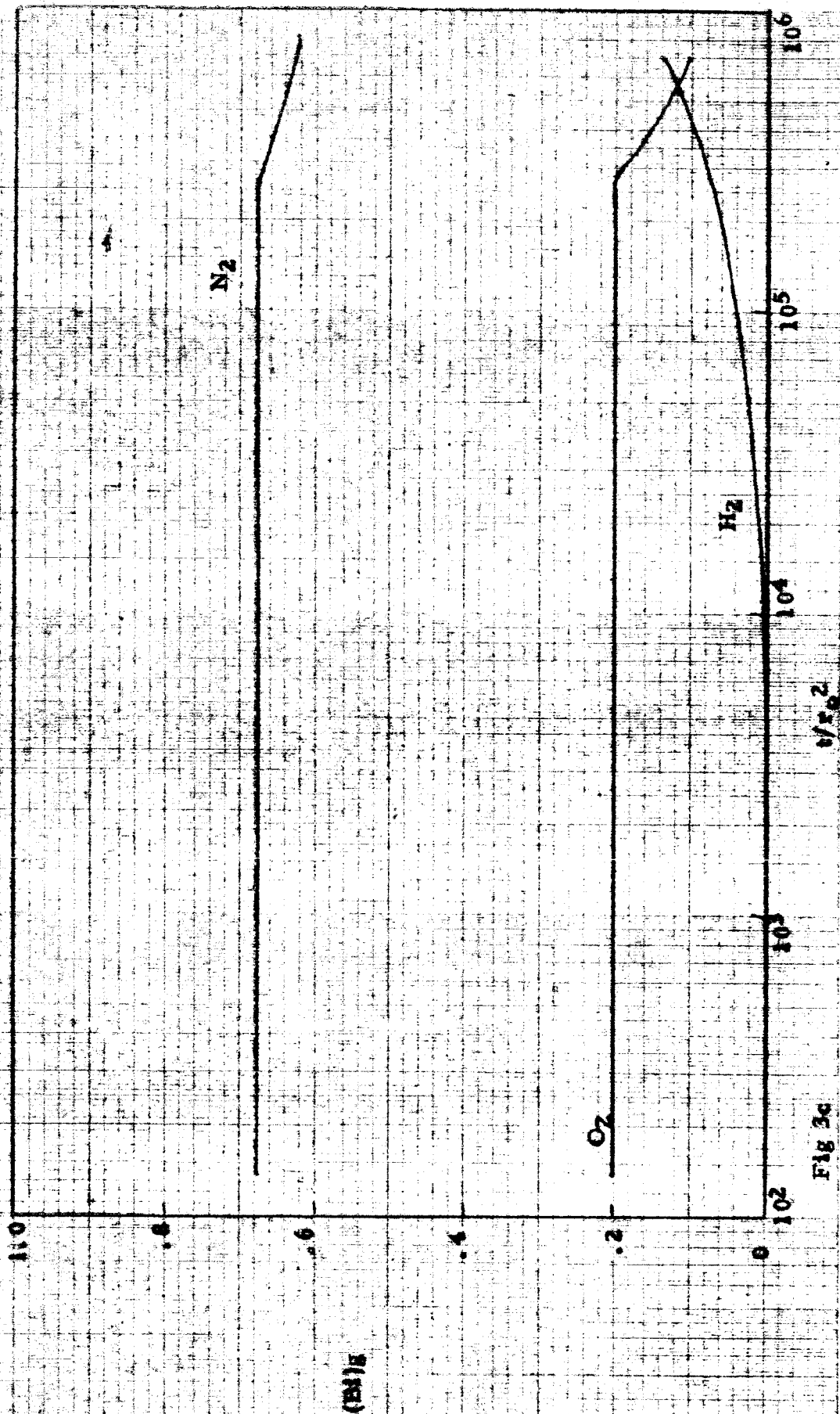


Fig 3c

Condensed Phase Mass Fractions vs  $t/\tau^2$

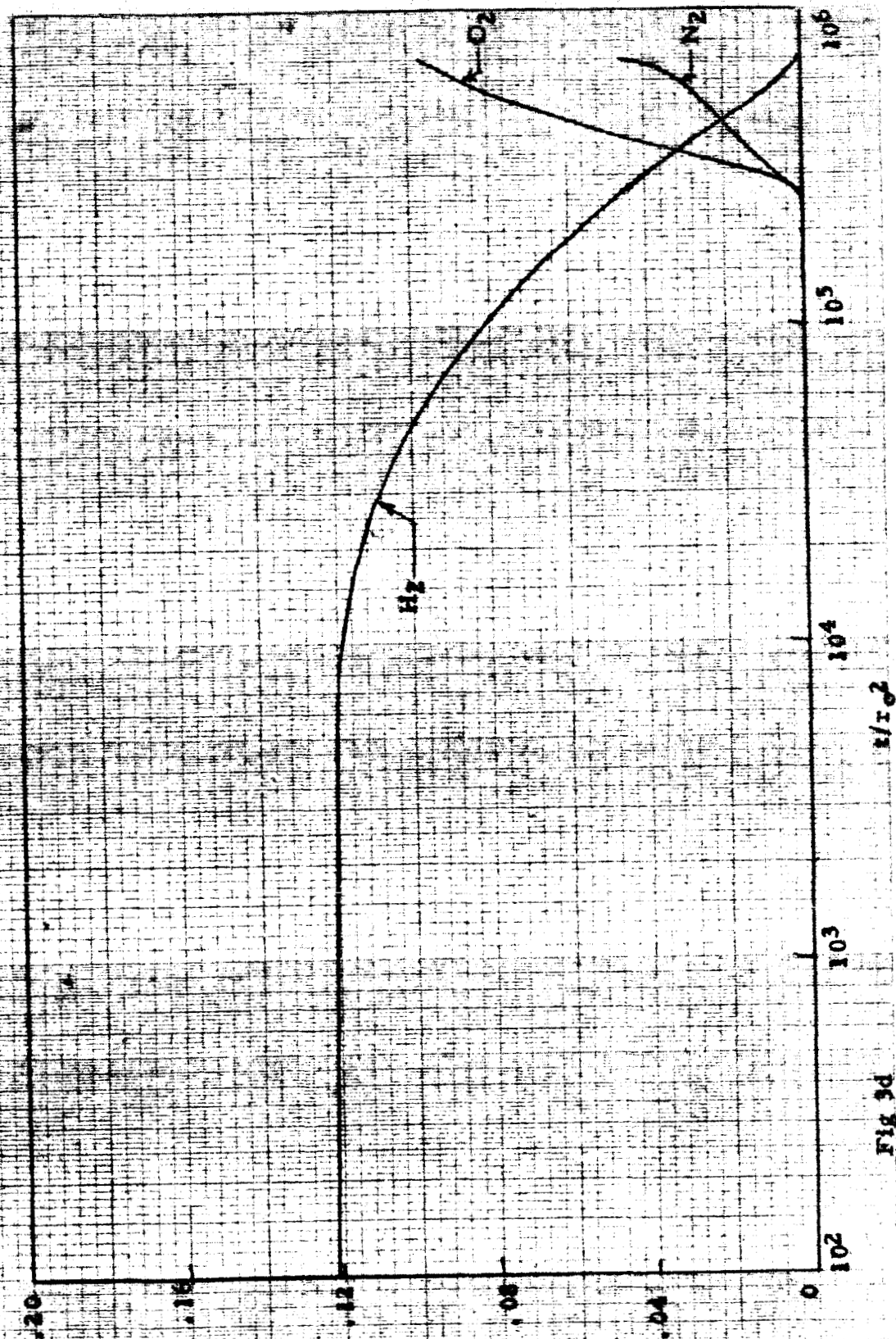


Fig 3d



Particle Radius and Degree of Vaporization vs  $t/r_0^2$

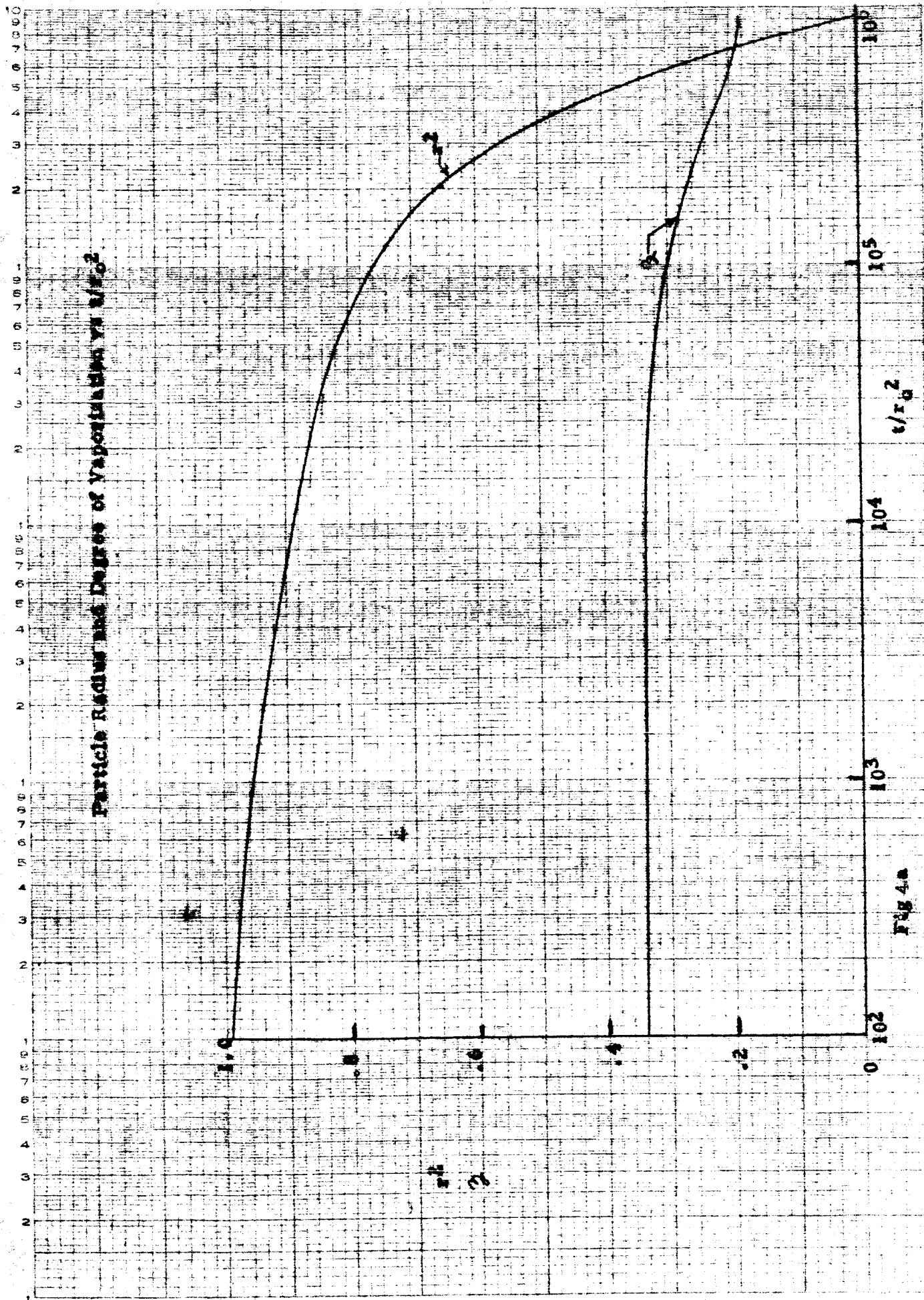


Fig 4a

Particle and Gas Temperatures vs  $t/\tau_0^2$

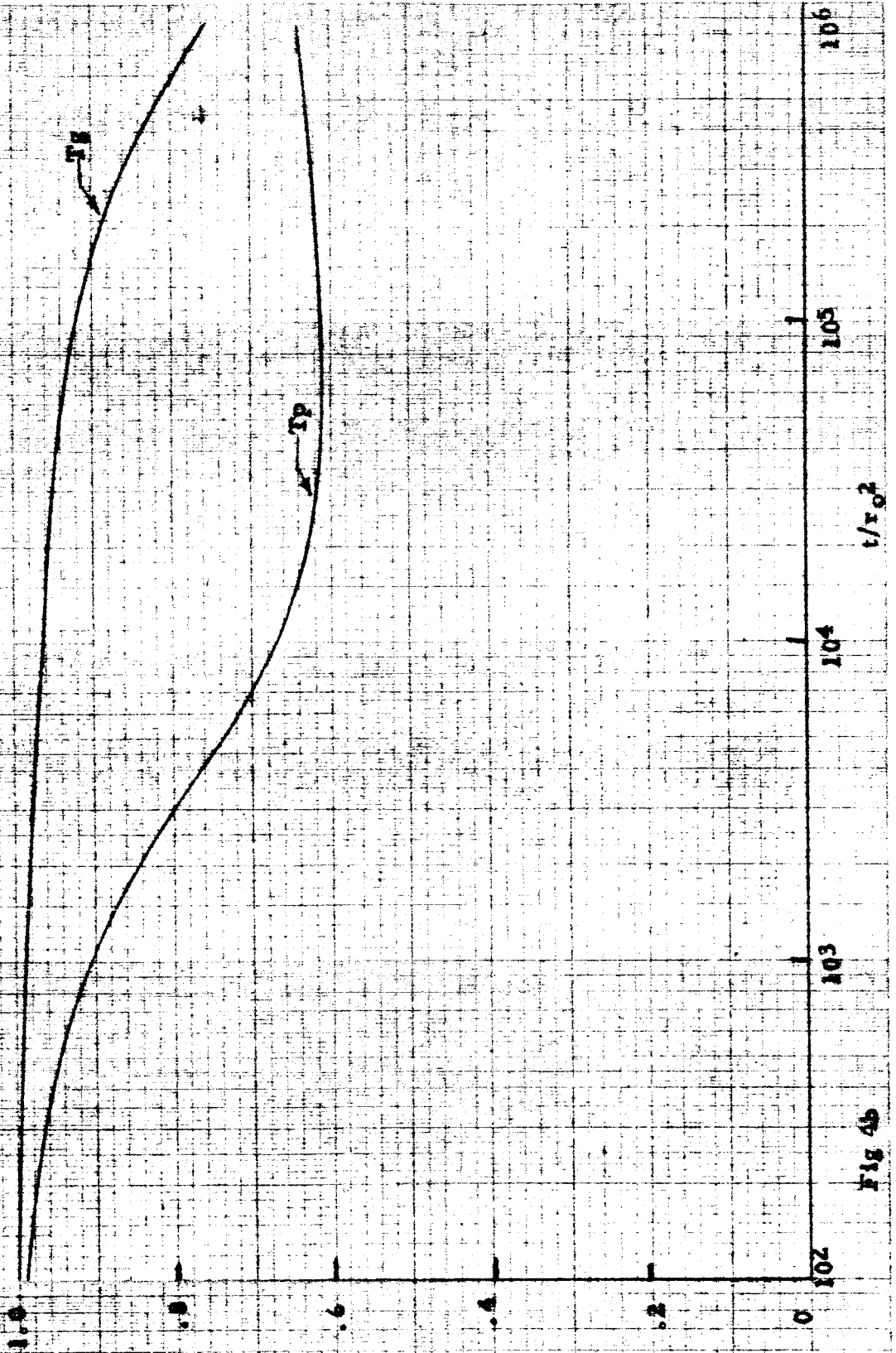


Fig 4b

Gas Phase Mass Fractions vs  $t/\tau_0^2$

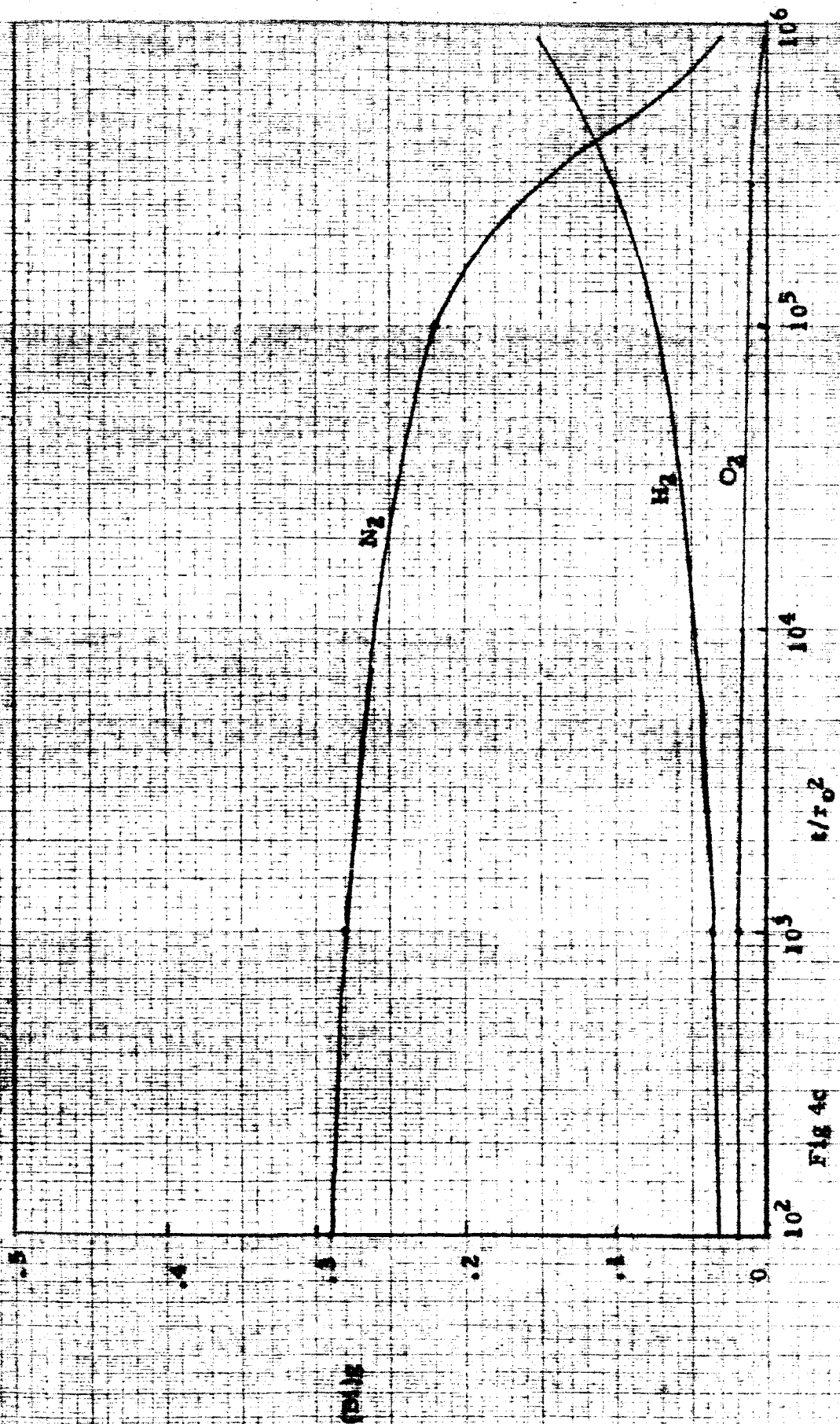


Fig 4c

5 CYCLES X 10 DIVISIONS PER INCH

Condensed Phase Mass Fractions vs  $t/\tau_0^2$

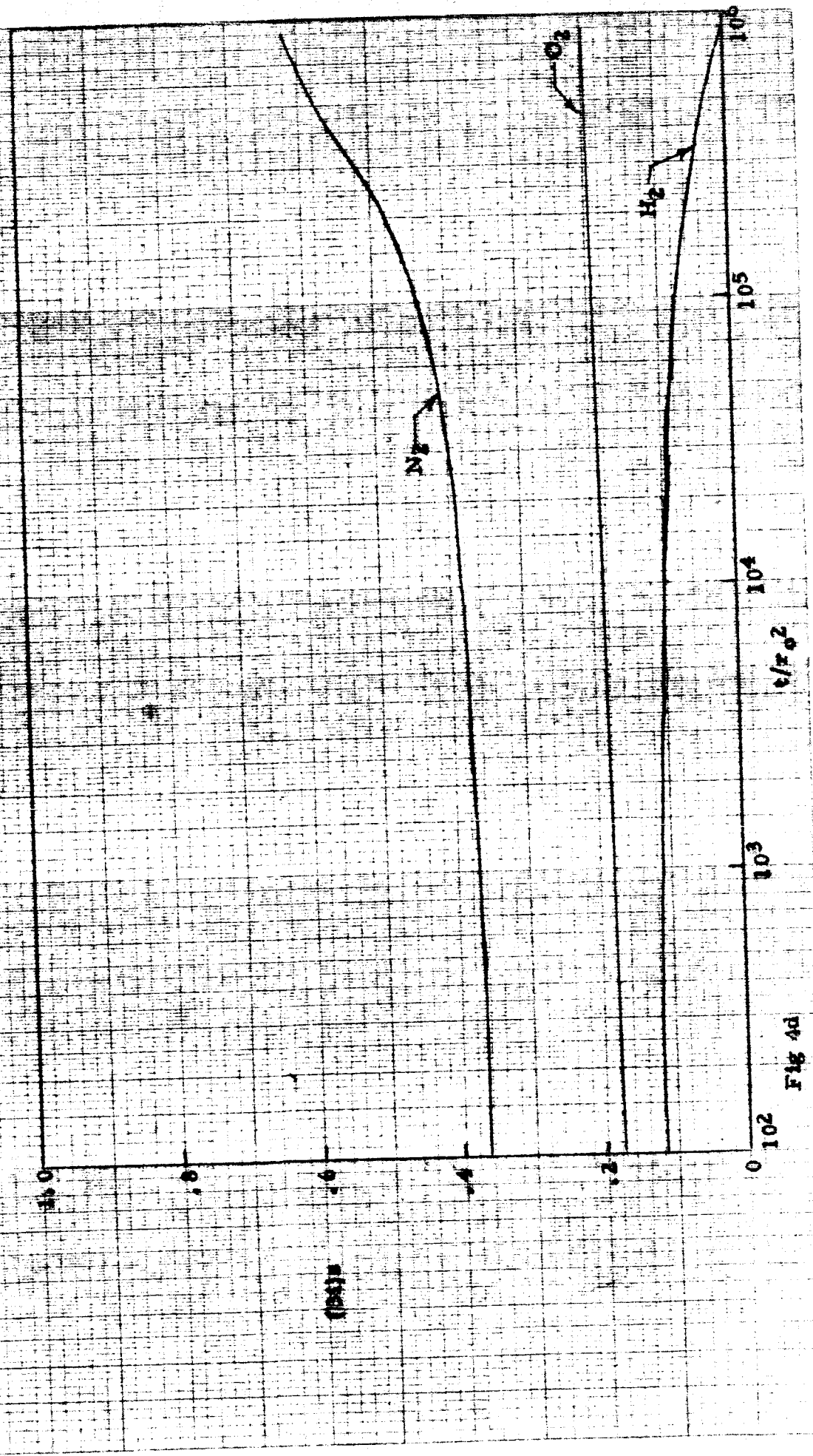


Fig 4d



Particle Radius and Degree of Vaporization vs  $t/r^2$

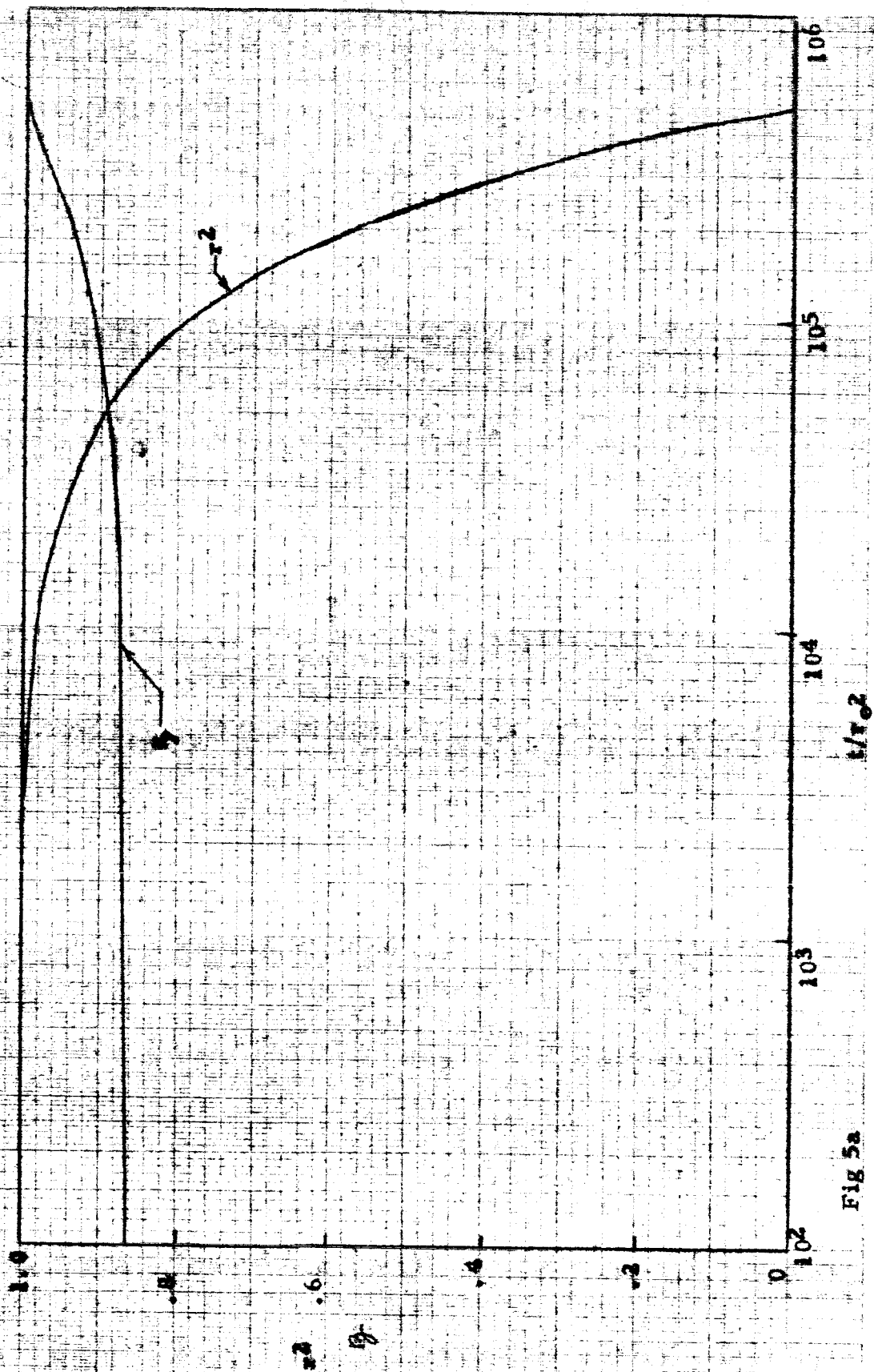


Fig 5a

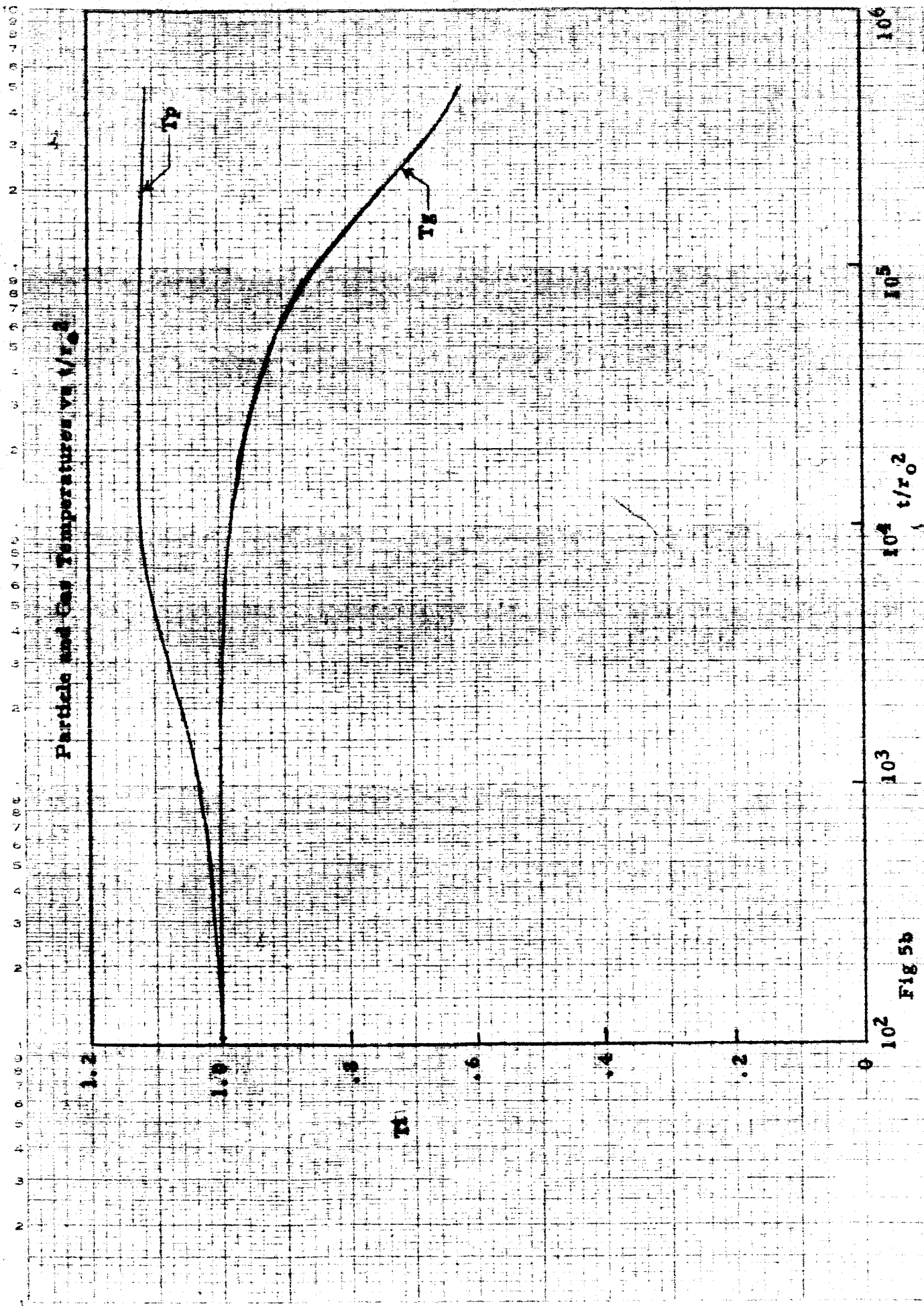


Fig 5b

Gas Phase Mass Fractions vs  $1/x_0^2$

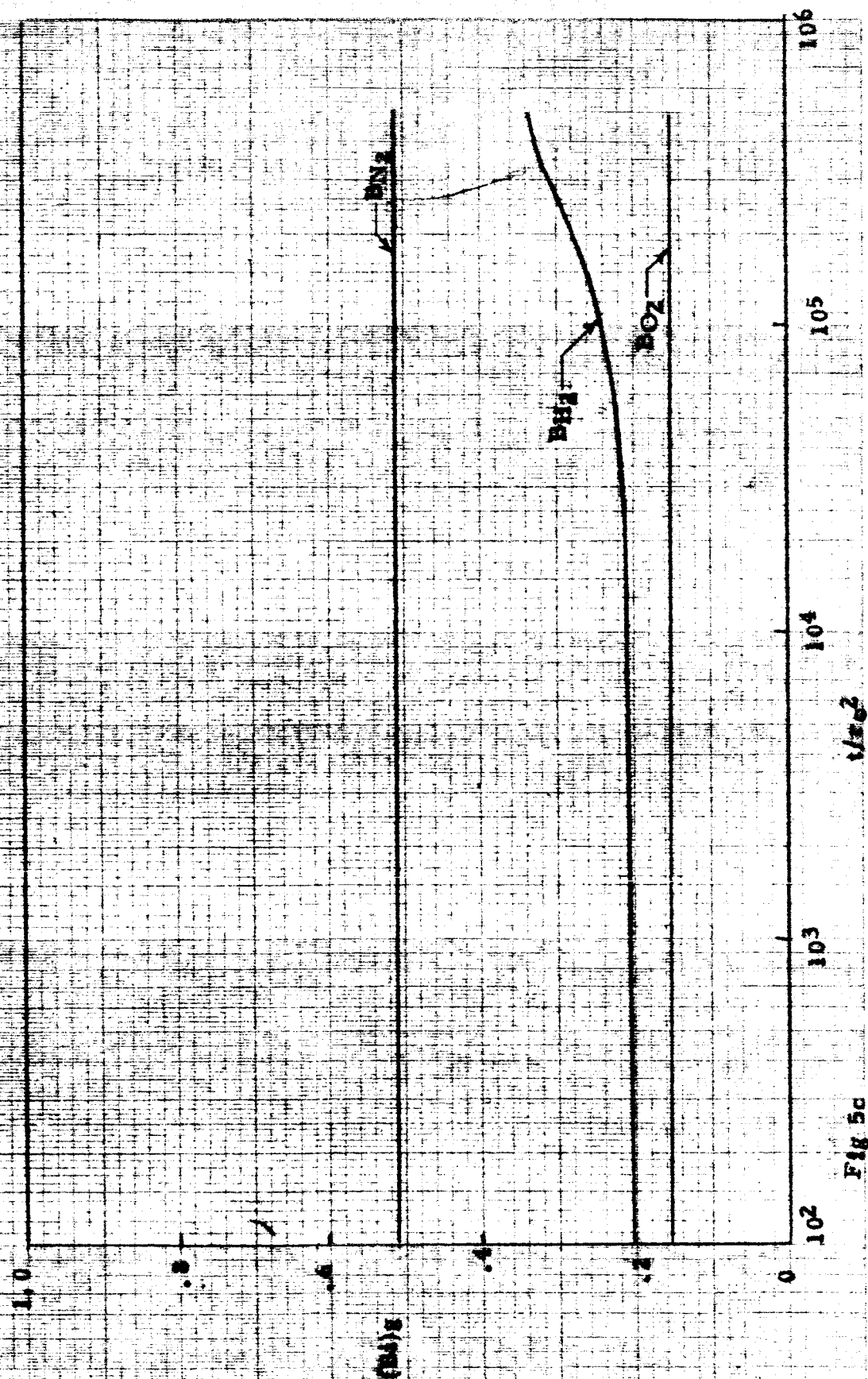
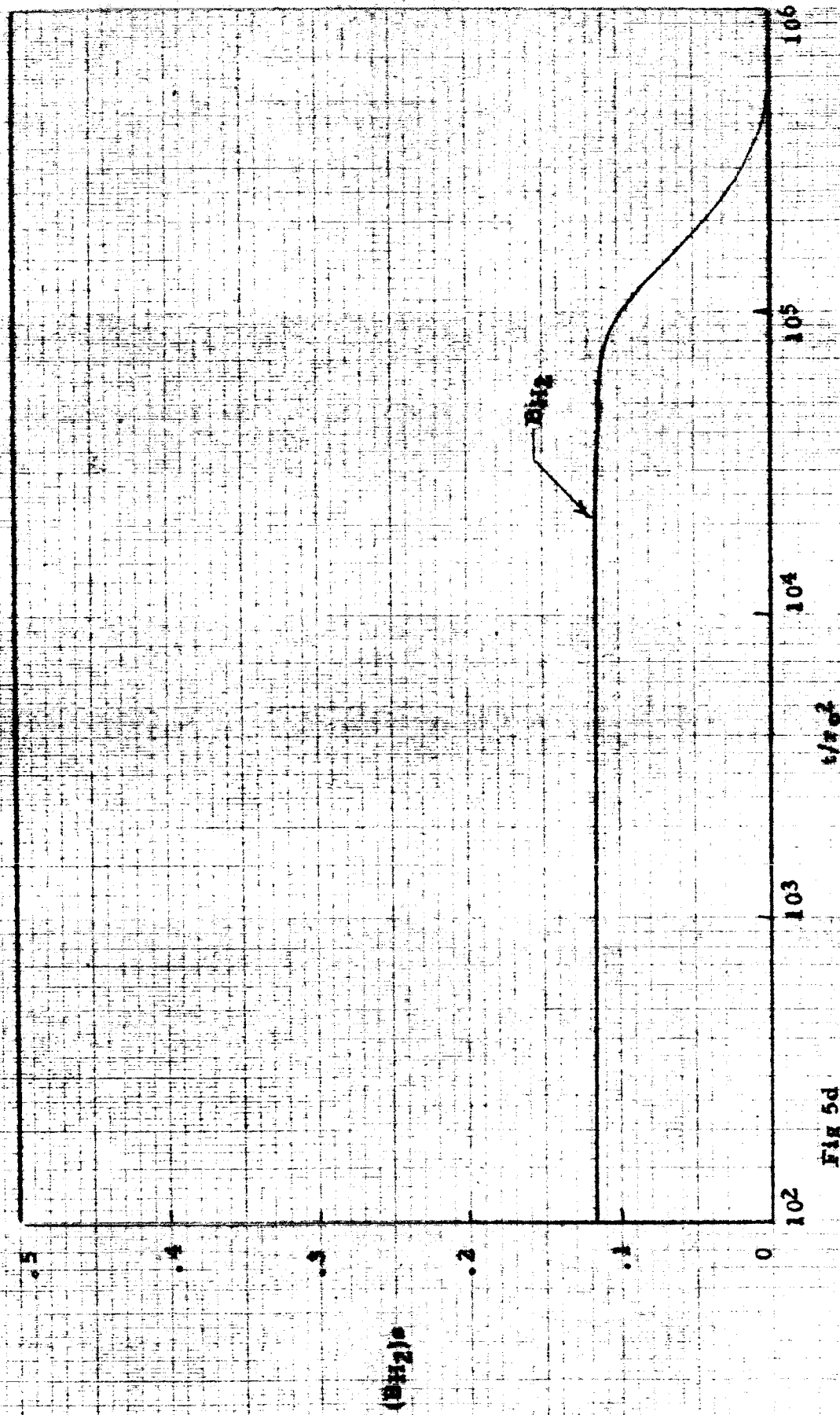


Fig 5c

Condensed Phase Mass Fractions vs  $t/\tau_0^2$



Particle Radius and Degree of Vaporization vs  $t/r_0^2$

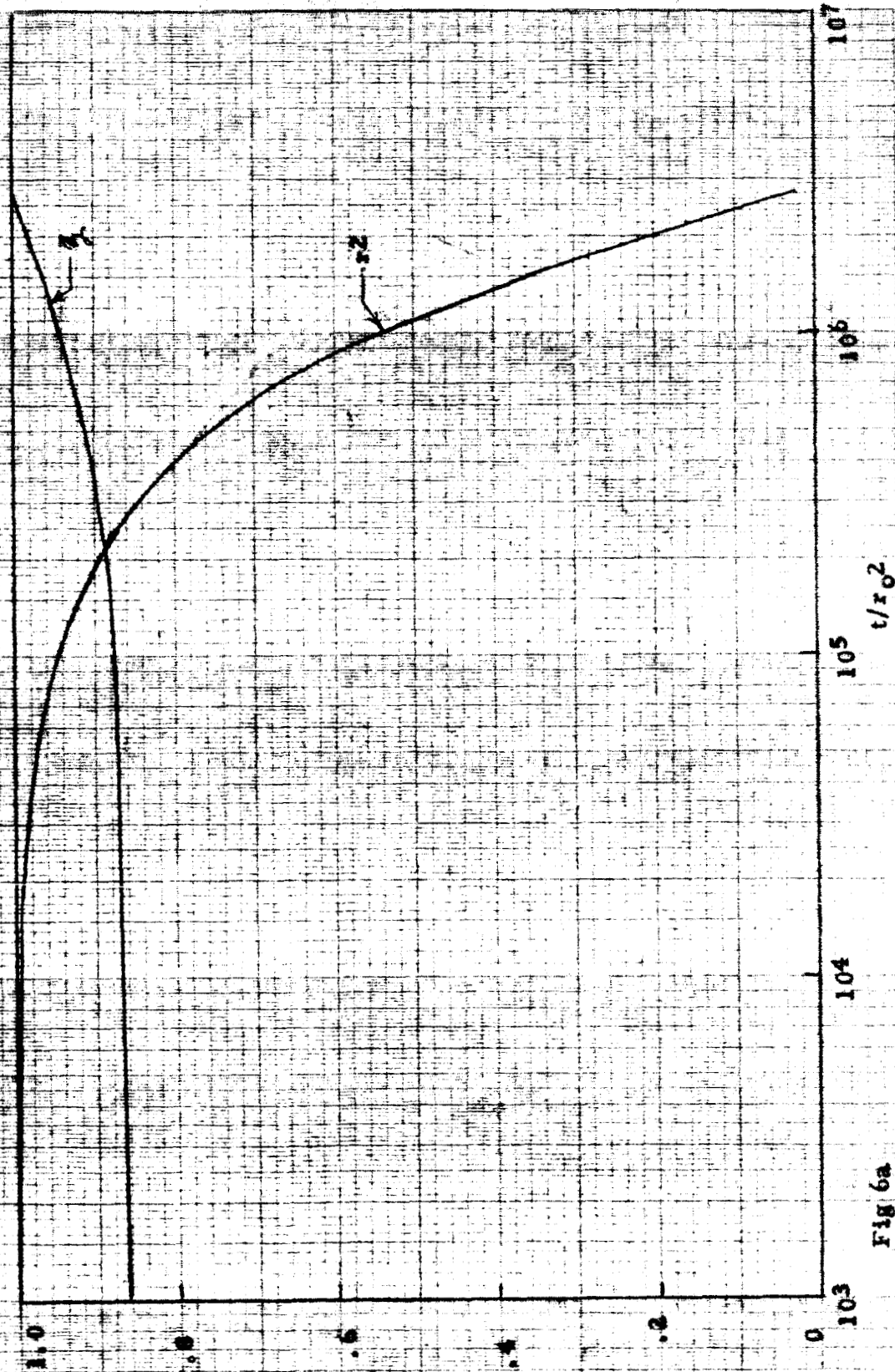


Fig 6a



Particle and Gas Temperatures vs  $t/r_0^2$

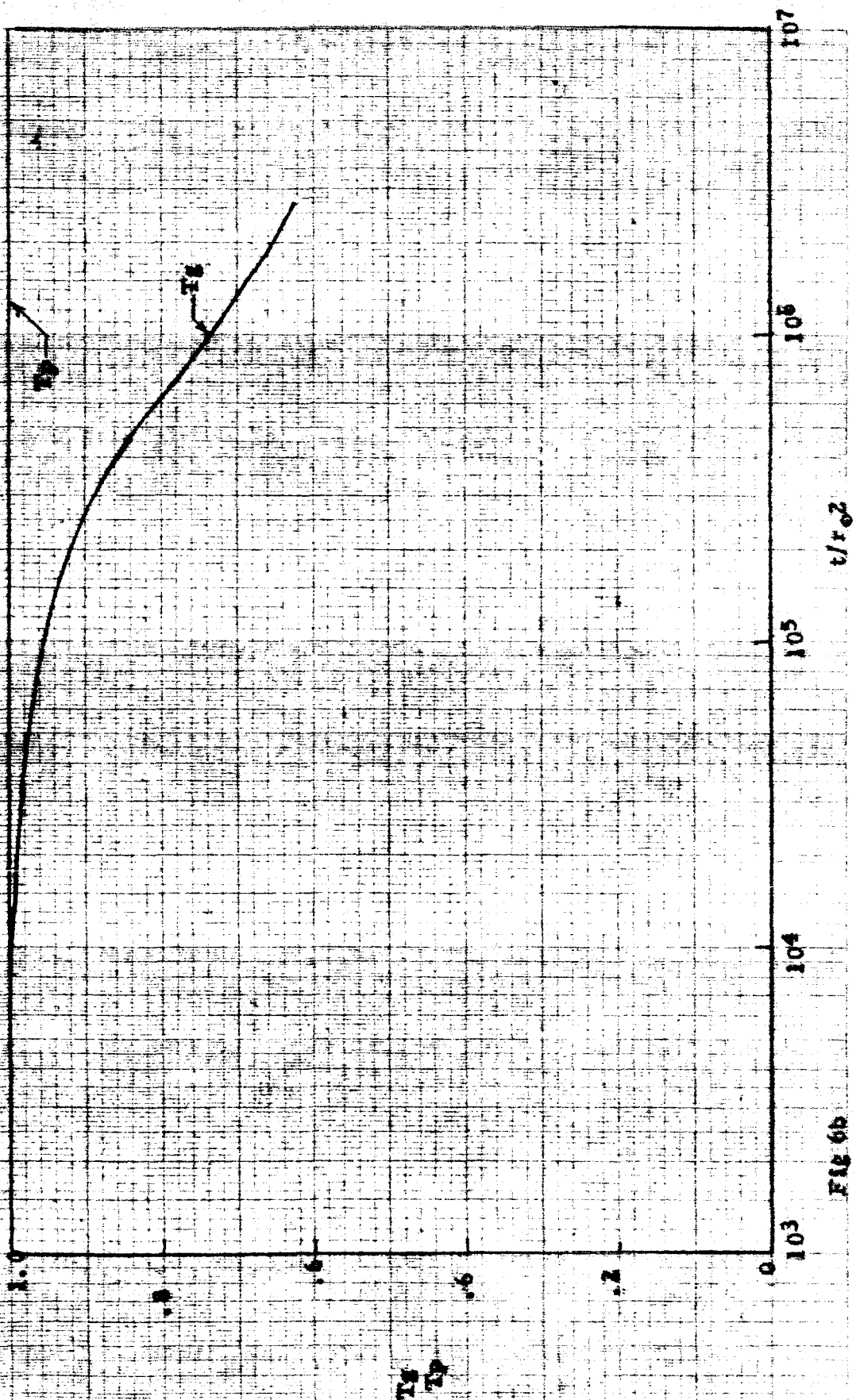


Fig 6b

Gas Phase Mass Fractions vs  $t/\tau_0^2$

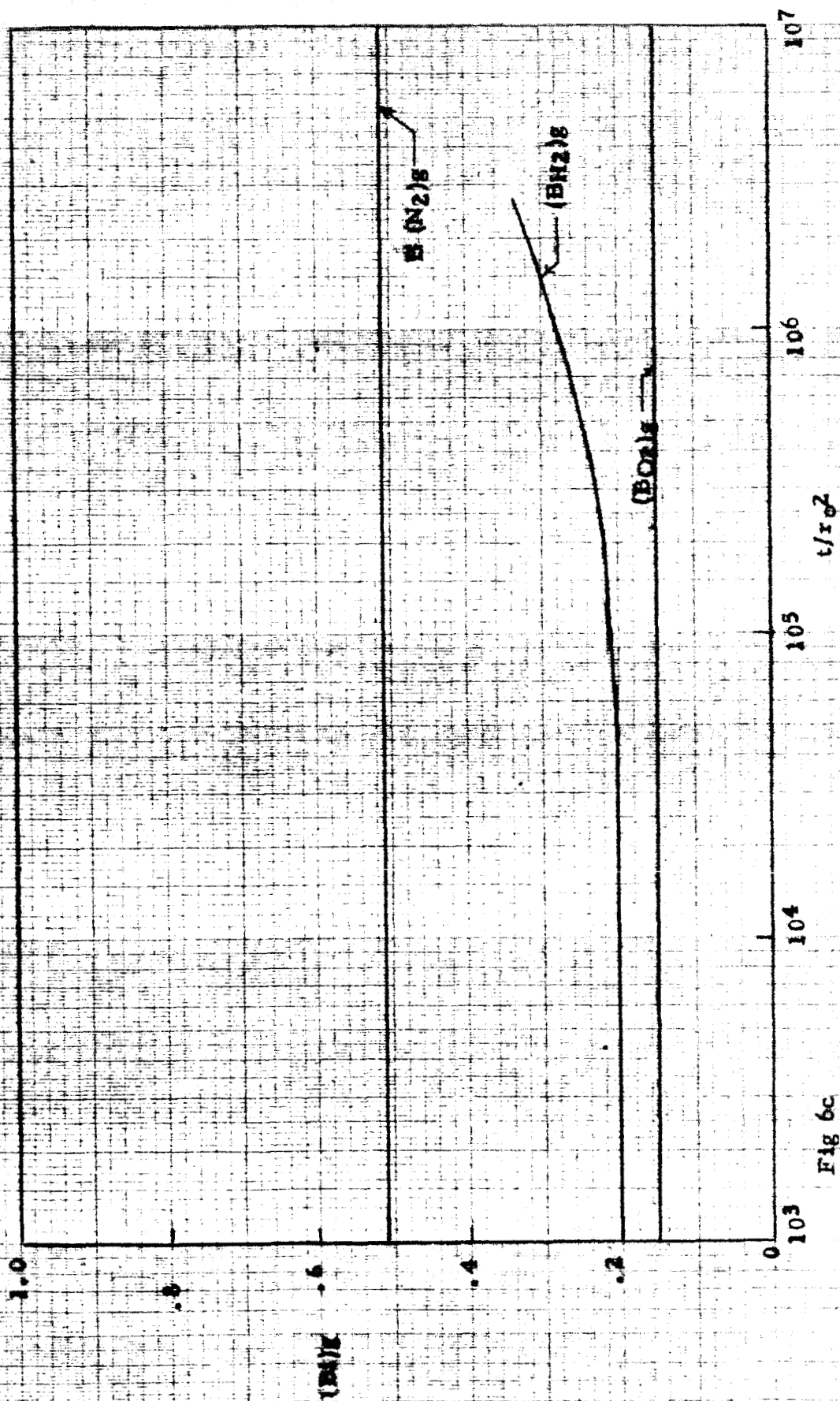


Fig 6c

Condensed Phase Mass Fractions vs  $t/\tau_0^2$

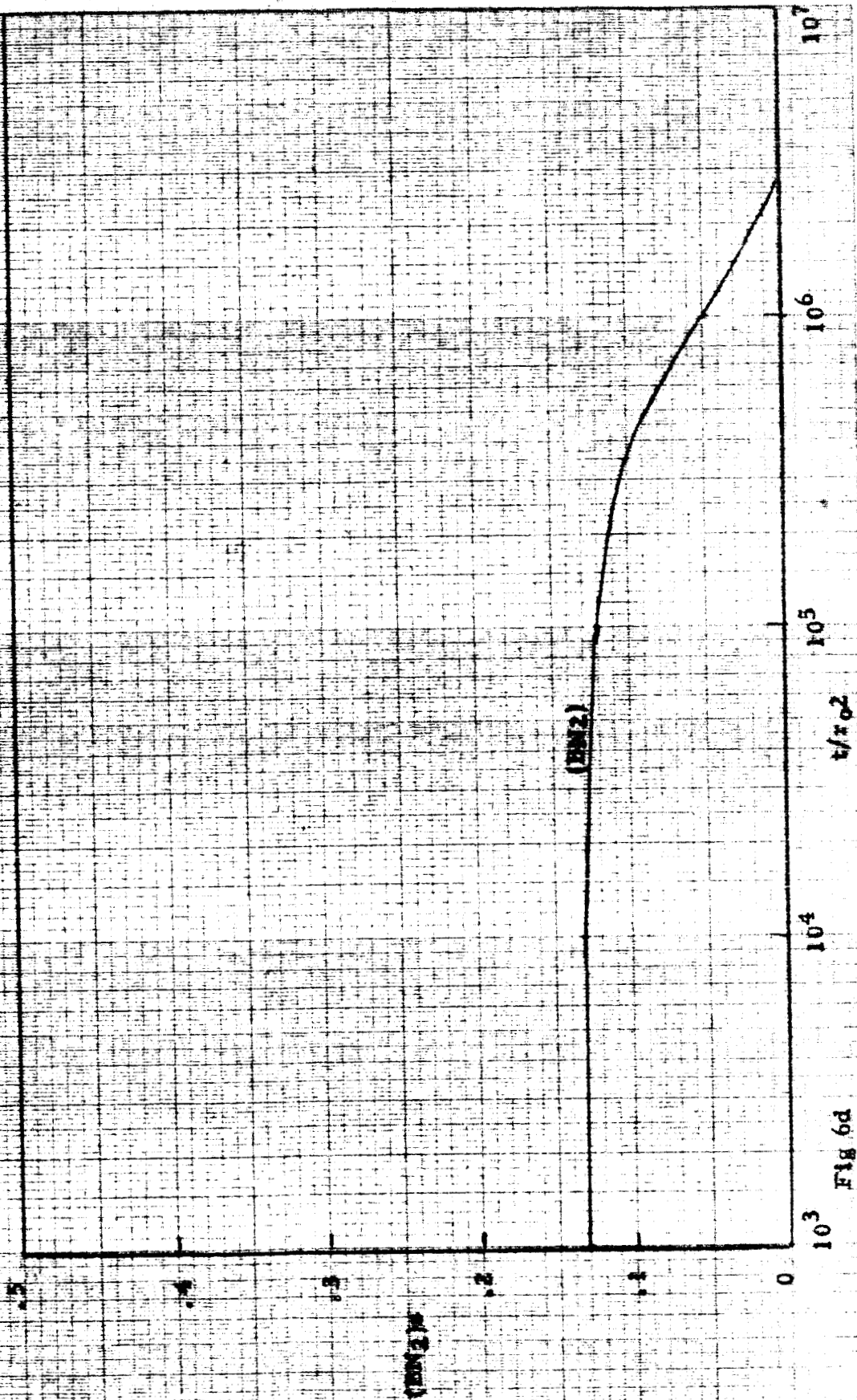


Fig 6d



Particle Radius and Degree of Vaporization vs  $t/\tau_0^2$

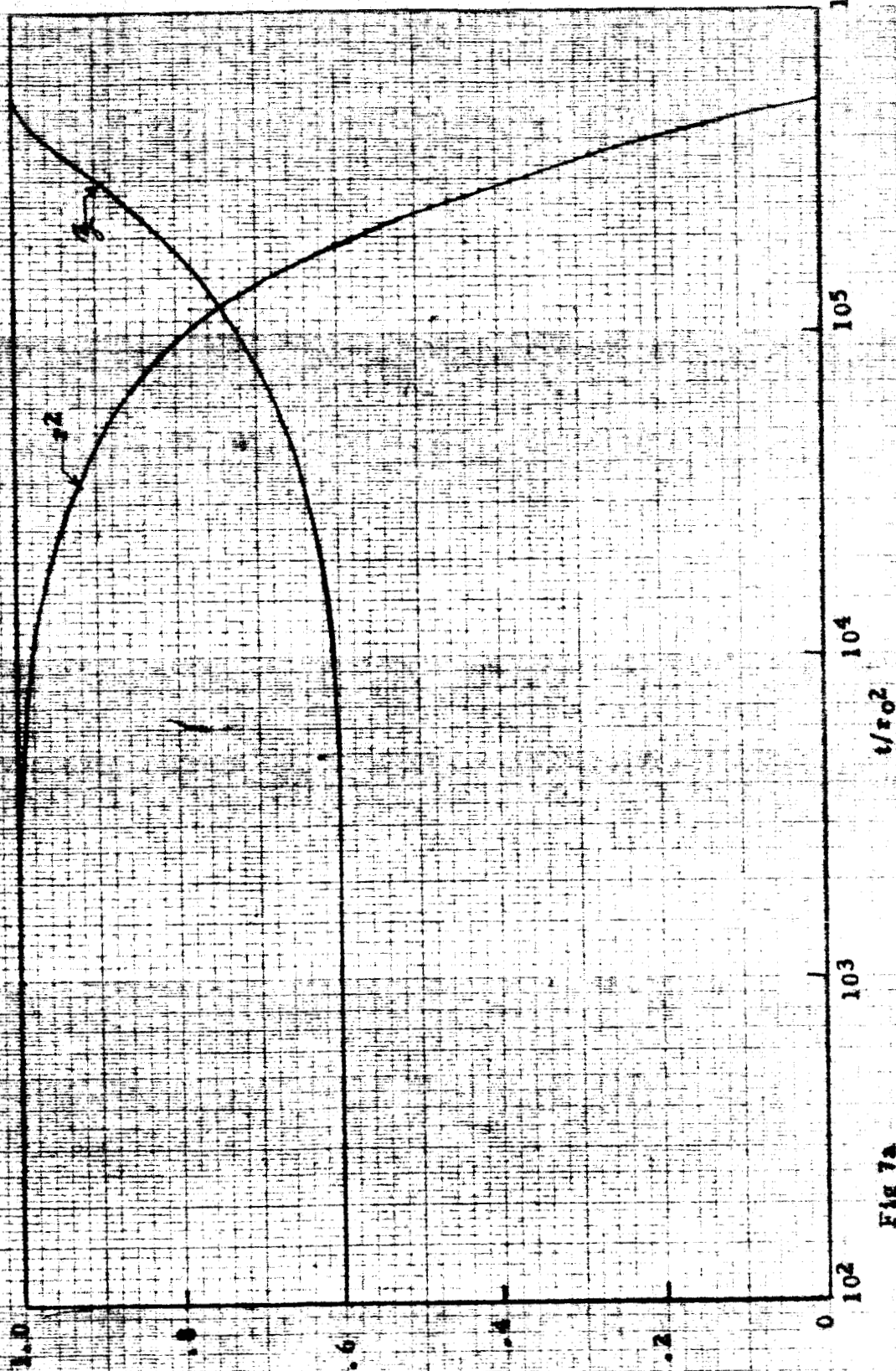


Fig 7a

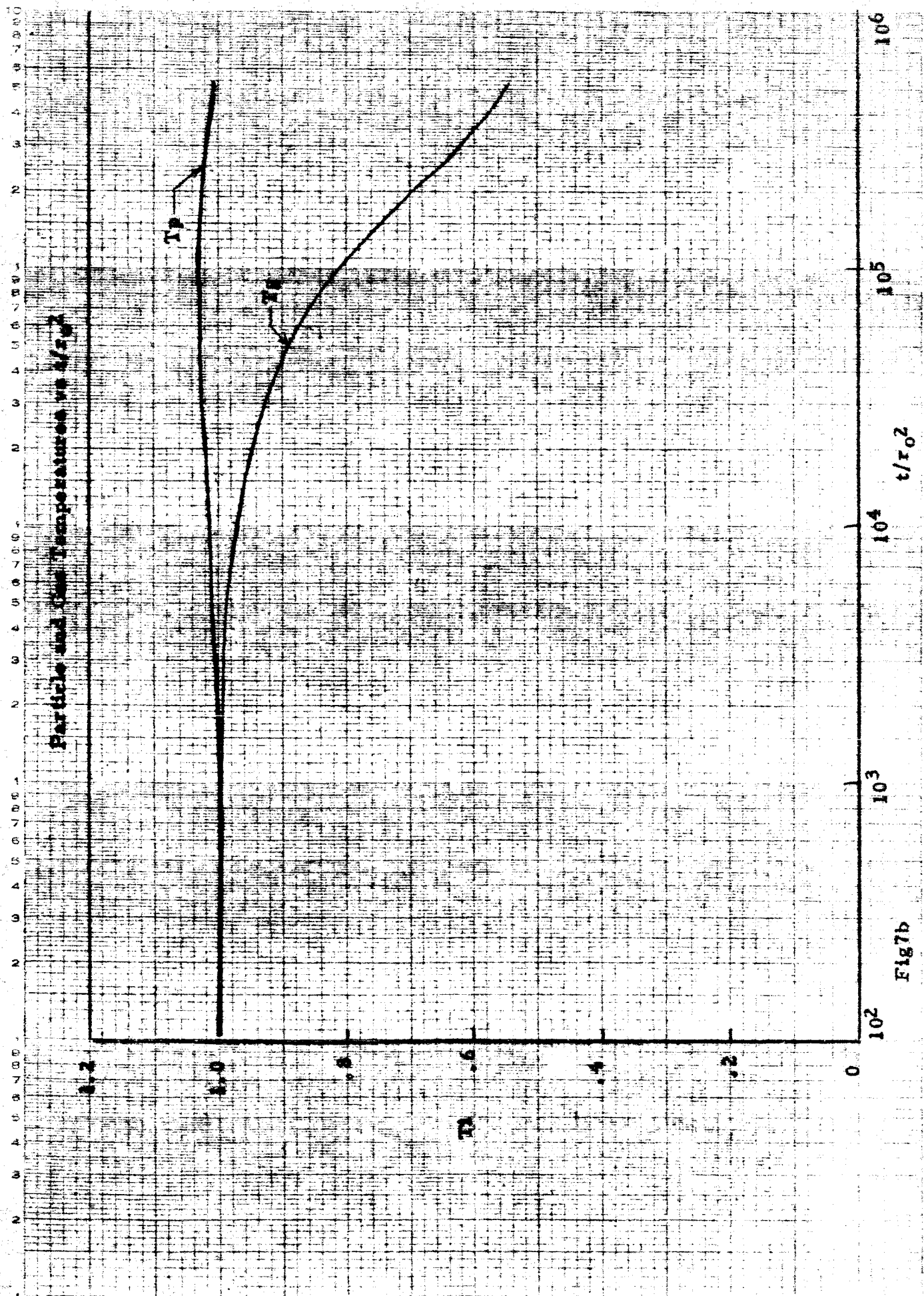


Fig7b

Gas and Condensed Phase Mass Fractions vs  $t/r_0^2$

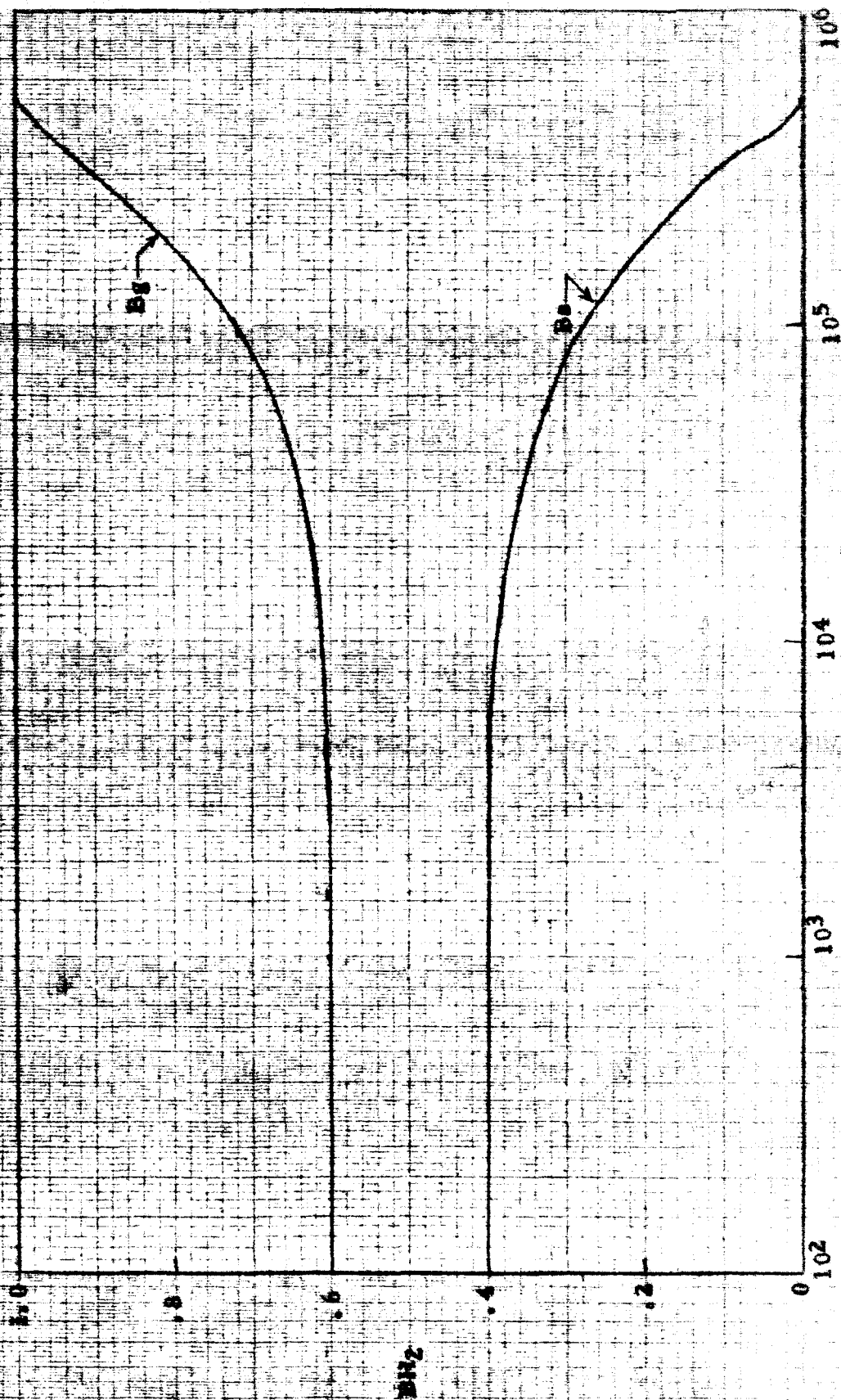


Fig 7c

Particle Radius and Degree of Vaporization vs  $t/r_0^2$

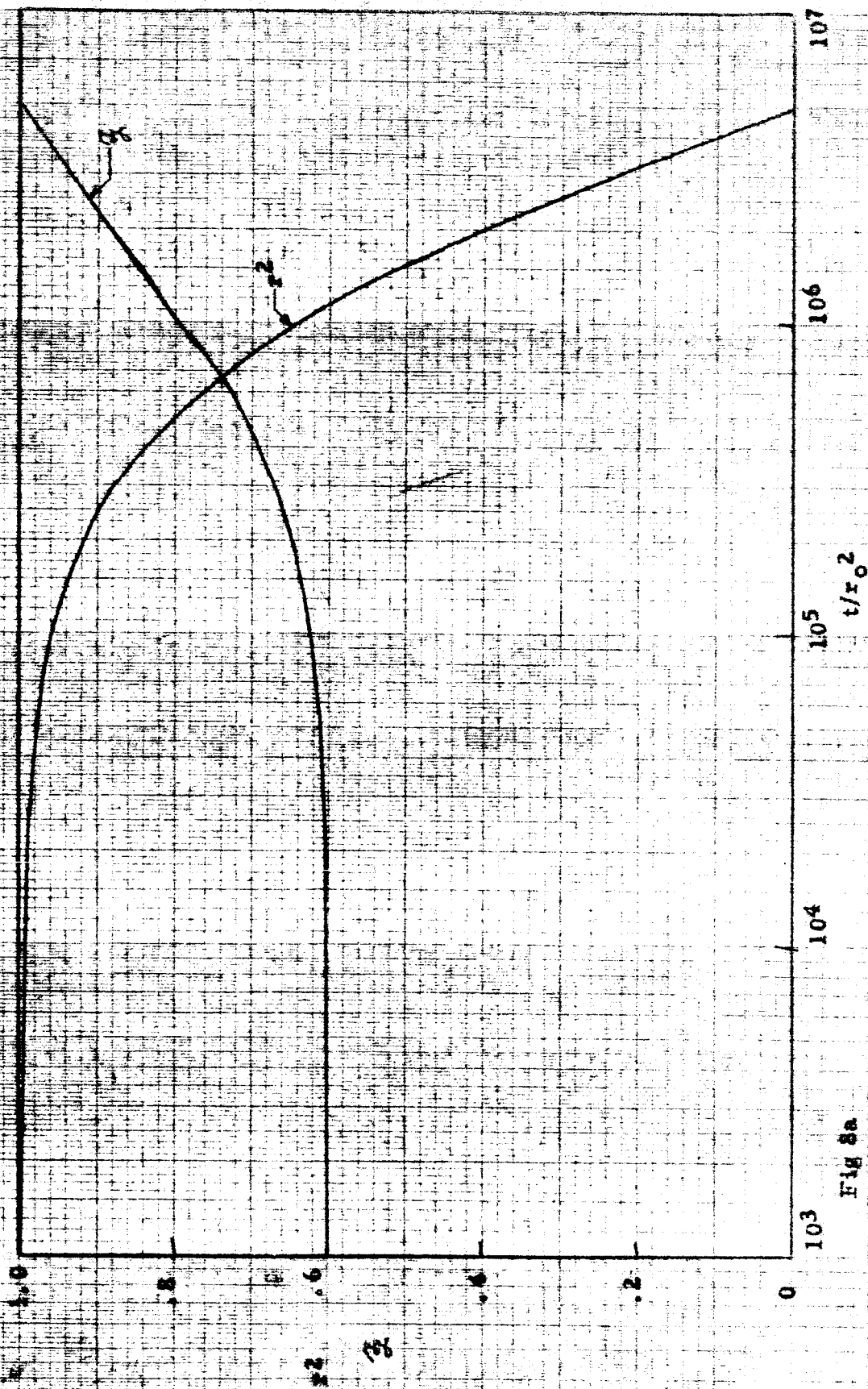


Fig 8a



Particle and Gas Temperatures vs  $t/\tau_0^2$

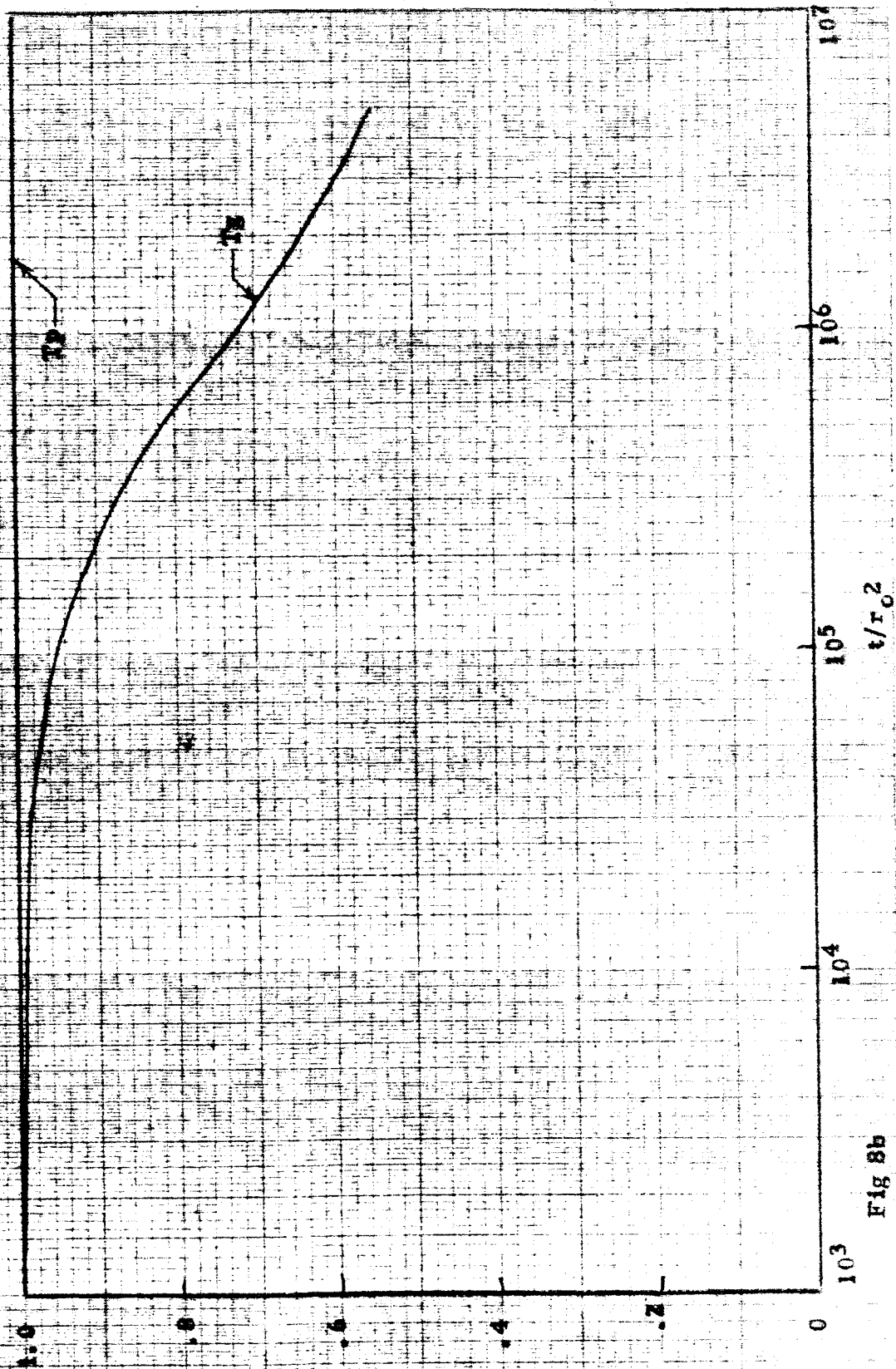


Fig 8b

Gas and Condensed Phase Mass Fractions vs  $t/\tau_0^2$

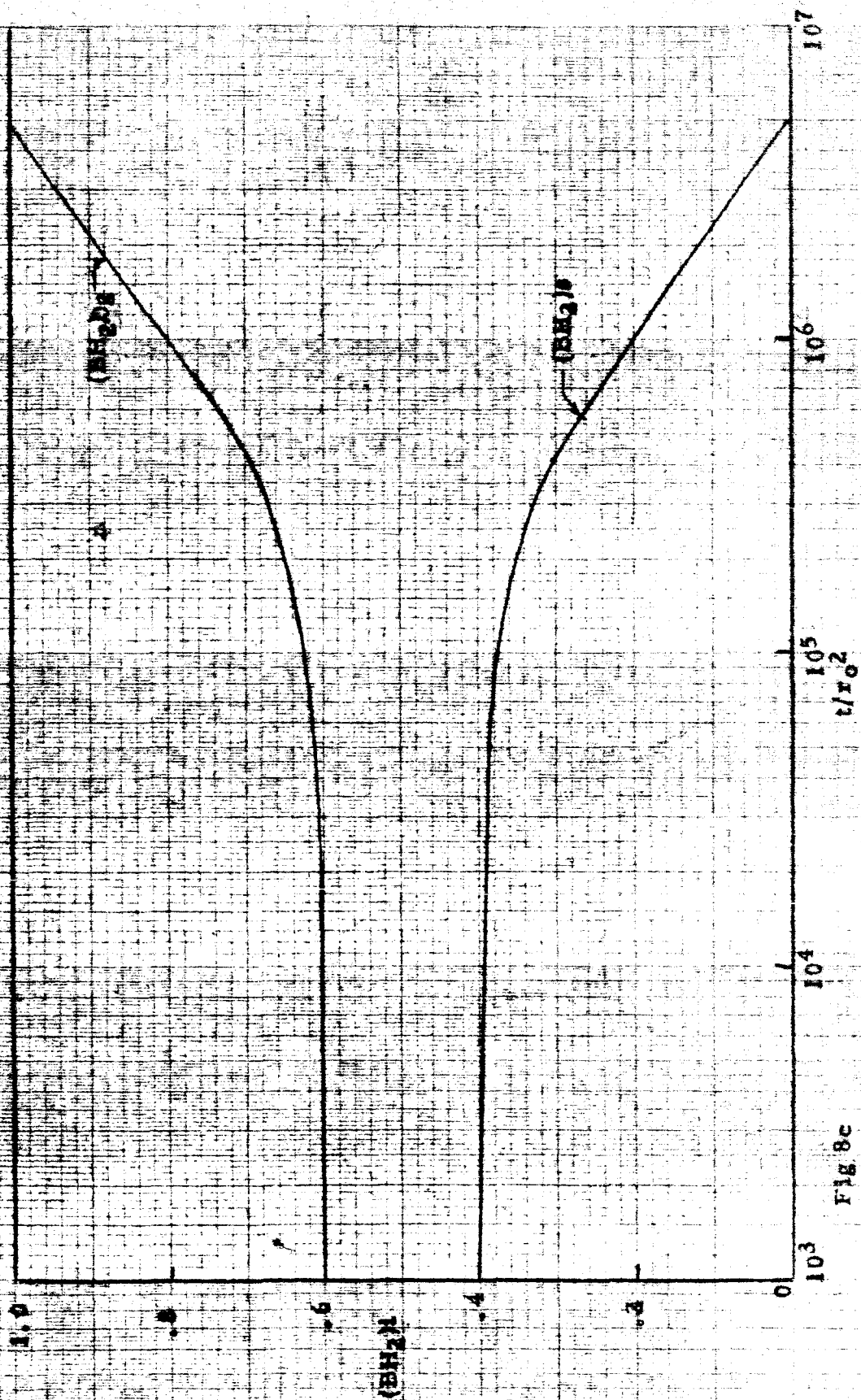


Fig 8c